

The Nature and Origin of Mass Spectral Peaks

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by

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## Summary

In Chapter one, a general review of mass spectrometry was made in which the history of mass spectrometry was traced from the discoveries of Goldstein and Wien to J.J. Thomson's first mass spectrograph and Aston's first mass spectrometer. The evolution and improvement in these early instruments was followed by reference to the work of Barber and Stephens, Nier, Herzog and Mattauch for the development of double-focusing instruments. Other types of instruments such as the dynamic instruments, have also been mentioned.

Methods of ionisation and systems of sample introduction were described, as were the uses of mass spectrometry in analytical chemistry, both qualitatively and quantitatively, and in other branches of science. Automatic data acquisition, reduction and processing techniques, including precise mass measurement, were mentioned.

Several theories useful in the interpretation of mass spectra were considered.

The types of ions formed in the mass spectrometer were indicated and particular emphasis was placed on the use of metastable ions as a source of information to the organic mass spectroscopist. In addition, the relevance of thermochemical measurements, isotopic labelling, substituent effects, ion-molecule reactions and chemical ionisation to ion structure determination was discussed.

In Chapter two, a new method of precise mass measurement of ions by mass spectrometry was described, and compared with methods used in the past by other workers. These ranged from the classical peak matching technique to the first semiautomatic process developed by Biemann and finally to other more advanced automatic processes for both electrical and photographic recording, using on or off-line systems. The new mathematical method used, spline-fit interpolation was shown

to yield results which were as accurate as the results obtained by the basic automatic method of Biemann; moreover, it had several advantages in its simplicity and applicability to both electrical and photographic recording systems.

In Chapter three, the shape of the peaks in a double-focusing mass spectrometer in slow scans was studied. The mathematical treatment and the results showed that the peaks can be considered triangular. The calculation of the areas of the peaks accordingly became an easier task than if they were calculated using the planimeter, even in a digitisation treatment.

In Chapter four, a review of ionisation phenomena was made. The definitions of ionisation and appearance potentials were given and methods for their calculation critically reviewed. Ways in which thermochemical data and structural details may be elucidated from these data were described.

The ionisation and appearance potentials for the positive ions of methanol, deuterated methanol and ethylene glycol and their fragments were calculated from experimental data acquired by electron-impact on the neutral molecule.

Thermochemical data and structural details derived from these observed values were discussed, and a compelling argument leading to the conclusion that the structure of the ion  $\text{CH}_3\text{O}^+$  is in fact  $\text{CH}_2\text{OH}^+$  was presented.

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CONTENTS

Page

Chapter 1.	<u>Introduction</u>	1
	Bibliography	13
Chapter 2.	<u>The determination of the masses of the ions by spline-fit interpolation</u>	
2.1.	Introduction	20
2.2.	Theory	32
2.3.	Experimental and Results	39
2.4.	Discussion of Results	106
	Bibliography	108
Chapter 3.	<u>The Shape of Mass Spectral Peaks</u>	
3.1.	Introduction	112
3.2.	Theory	114
3.3.	Experimental and Results	117
3.4.	Discussion of Results	129
	Bibliography	131
Chapter 4.	<u>The determination of ionisation potentials and bond dissociation energies of some organic compounds</u>	
4.1.	Introduction	132
4.2.	Experimental and Results	147
4.3.	Discussion of Results	158
	Bibliography	164

## Chapter 1.

Introduction

The history of mass spectroscopy can be traced back to 1886 when the "canal rays" were discovered by Goldstein <sup>1</sup>.

Subsequently W. Wien<sup>2</sup> in 1898 proved conclusively that the rays were positively charged by observation of their deflection in magnetic and electric fields.

Meanwhile J.J. Thomson<sup>3</sup> in 1910 built the first mass spectrograph, which did not give a focused ion beam. In his apparatus a beam of positive ions was produced by an electrical discharge in a gas at reduced pressure. These ions, of varying mass and energy, were accelerated towards a collimator and subsequently passed through uniform parallel electric and magnetic fields perpendicular to the direction in which the ions entered them. After deflection each ion described a parabola recorded on a photographic plate, the position of any ion on this parabola being a measure of its momentum. With this apparatus Thomson showed the existence of two neon isotopes.

The founder of modern mass spectroscopy was F.W. Aston<sup>4</sup>, who, in 1919, introduced an instrument with consecutive electrostatic and magnetic fields. The lines of focus of ions of different mass-to-charge ratio lay on a plane and so a photographic plate could be used to record the mass spectrum. This type of apparatus is best suited for the accurate determination of isotopic mass.

The first mass spectrometer, constructed by Dempster<sup>5</sup>, appeared about the same time. The separation of the ions was achieved by varying the accelerating potential of the ions prior to their entry into a 180 degree uniform magnetic field. The ions were collected, one species at a time, in a Faraday cup<sup>6</sup>.

When the technique involved for registering ions is a photographic emulsion, the term mass spectrography is used; when it is a successive

electronic recording of the individual ion currents, mass spectrometry is common<sup>7</sup>.

Both Aston's mass spectrograph and Dempster's mass spectrometer had only single-focusing properties. The former had velocity focusing and by analogy with optics the magnetic field was used like an achromatic prism. In the latter there was direction focusing, the magnetic field being used like a lens.

In Dempster's instrument, since there was no velocity focusing, it was necessary to use an ion source which provided a monoenergetic beam. The accuracy of mass measurement obtained with an instrument of this type is lower than Aston obtained and therefore it is more suitable for ion abundance measurements, since it measures the ion currents electrically.

In these early instruments resolution (1) was low, and in the years that followed Dempster and Aston's discoveries the development of these instruments continued as investigators tried to achieve a better way of focusing the ion beam and thus improve resolution and sensitivity (2).

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(1) Resolution<sup>8</sup> or resolving power is usually defined as the largest mass at which two adjacent peaks of equal height, differing by one unit of mass, exhibit a valley not greater than a certain percentage (usually 10%) of the peak height. The resolution of a mass spectrometer is a measure of its ability to separate ions of one mass from those of a slightly different mass.

(2) Sensitivity<sup>9</sup> measures the response of an instrument to ions of a particular component at an arbitrary mass over charge ratio. The response is measured by charge received in a measuring device or blackening of a photographic plate.



Barber<sup>9</sup> and Stephens<sup>10</sup> in 1933 showed that operation of a mass spectroscope with a 180 degree magnetic sector was only a special case of focusing action for any wedge-shaped magnetic field. They proved that when the ion beam, homogeneous in mass and energy, enters and leaves the field at right-angles to the field boundary, it is focused on the line passing through the point of origin of the ions and the apex of the magnetic field. For several years after the publication of their work, no sector-type mass spectrometers were built. Then, in 1940, Nier<sup>11</sup> reported the construction of a 60 degree sector instrument, and following the initial instrument a number of spectrometers employing different sector angles<sup>12</sup> were constructed. In the modern mass spectrometers, the choice of sector angle is governed by several factors.<sup>12</sup>

Meanwhile other methods of analysing beams of positive ions were being developed<sup>13</sup>. These methods used crossed electrostatic and magnetic fields.

In modern instruments, as a result of the better design, and of the use of electron multipliers<sup>14</sup> as more sensitive collecting devices, a resolution of 10,000 can be attained<sup>15</sup>, a great improvement over the 100 resolution in Dempster's instrument. Single-focusing mass spectrometers are very much used in chemical analysis.

Instruments which incorporate the two principles of velocity and direction focusing are known as double-focusing instruments. The complete theory of achieving double-focusing using a radial electrostatic and a homogeneous magnetic field was developed by Herzog<sup>16</sup> and Mattauch<sup>17</sup>. Double-focusing instrumentation can be classified into four main categories:

(i) The Mattauch-Herzog geometry<sup>18</sup>.

This design employs consecutive electrostatic and magnetic fields which deflect the ion beams in opposite directions. The ions come to focus in the same plane, where they are usually recorded on a photographic plate. Its focusing properties are of first order for all masses. The

commercial versions of this design are commonly used for chemical analysis with a resolution of several thousands and for analysis of inorganic solids with a spark source.

(ii) The Nier-Johnson geometry<sup>19</sup>.

A 90 degree electrostatic deflection is followed by a 60 degree magnetic deflection and the spectrum is scanned by varying the electrostatic field. The ion beam is deflected in the same direction and the ions are focused at the intersection of the velocity focusing curve with the direction focusing curve. The two main commercial versions of this design are used primarily for high-resolution spectra of hydrocarbons and other organic compounds.

(iii) The trochoidal path mass spectrometer.

Using crossed homogeneous magnetic and electrostatic fields, Eleakney and Hipple<sup>20</sup> constructed an instrument that attained a perfect focus in the plane normal to the magnetic field. The path of an ion moving under such a combination of fields is a trochoid. The commercial versions of this instrument possess sufficient resolving power and sensitivity to be of value for analytical purposes.

(iv) The Dempster and Jordan-Bainbridge design.

The basic design created by Bainbridge and Jordan<sup>21, 22</sup> (based on the original design of Dempster) uses an electrostatic field with focusing properties corresponding to those in a semicircular magnetic field i.e. image and object images are zero. The mass scale in this spectrograph is linear.

Very high-resolution can be obtained with these double-focusing instruments at the expense of sensitivity<sup>23, 24, 25</sup>. They can attain a resolution of 1,000,000<sup>25, 26</sup>. Many methods of improving the focus, resolving power or intensity of the image obtained in mass spectrometers, both single and double-focusing, have been proposed and tried<sup>27</sup>.

The magnetic deflection instruments so far described are static mass spectrometers. There is, however, another type of instrument, in which a

time-dependent parameter is essential to the analysis of mass. The most common of these dynamic types is the time-of-flight mass spectrometer<sup>28</sup>. It was originally designed for the study of fast reactions, for which purpose it is well adapted owing to its capability of rapid scanning. The instrument effects mass separation of a pulse of ions of various masses and the same initial kinetic energy by the differences in flight time of ions of different mass when they are accelerated along a field-free tube. Currently, this type of instrument is used widely in the technique of combined gas chromatography-mass spectrometry.

Another important dynamic mass spectrometer is the quadrupole instrument<sup>29</sup>, which employs a radiofrequency field in conjunction with a static field. Other applications of radiofrequency techniques have been made to achieve mass separation in instruments of the Bennett<sup>30</sup> and Redhead types<sup>31</sup>. These instruments are generally of lower resolving power and mass range than those employing magnetic deflection, but as they have no magnet, they are generally less bulky. The omegatron<sup>32</sup>, the mass synchrometer<sup>33</sup> and the ion cyclotron resonance spectrometer<sup>34</sup> are also used.

Various methods may be employed to produce ions. The most common method is electron bombardment using sources of the efficient Nier<sup>11,35</sup> design. Other types of ion production, some of them finding increasing application, are thermal ionisation<sup>36</sup>, ion bombardment<sup>37</sup>, high voltage spark<sup>38</sup>, photon impact<sup>39</sup>, field ionisation<sup>40</sup> and chemical ionisation<sup>41</sup>.

Initially, sample inlet systems were available for handling only very volatile materials, but the introduction of heated inlet systems<sup>42, 43</sup> extended the range of compounds which could be examined. The use of a sintered glass disc covered with gallium was a standard heated inlet design for readily volatilised liquids. Although some solids can be introduced using the heated inlet system, in many cases

this is either impossible or leads to a spectrum of the pyrolysis products. The direct insertion of a sample of low volatility was developed to deal with these problems. Using this method<sup>44</sup> the amount of sample required can be as small as a nanogram ( $10^{-9}$  gm). It is obvious from this discussion that the method of introducing a particular sample to the mass spectrometer will depend on the chemical and physical properties of the sample as well as on the type of information required from the examination in the spectrometer.

The development of mass spectrometry and its use by industry was greatly promoted by the electronic advances which took place during the second world war. Mass spectrometry was first used for analytical purposes in the petroleum industry for the study of hydrocarbon mixtures in a quantitative way. The method<sup>45, 46</sup> of analysis developed depended on:

- (i) The reproducibility of the mass spectrum of a given compound under fixed operation conditions.
- (ii) The mass spectrum of a mixture being a linear superposition of the mass spectra of the components of the mixture.
- (iii) The direct proportionality of the sensitivity for the reference peak of a component to the partial pressure of that component in the mixture.

The qualitative analysis of mixtures of compounds has received much attention. Methods<sup>47</sup> have been developed to permit the identification of the components of a mixture when it is not possible to separate them readily by conventional analytical techniques.

The combination of gas-liquid chromatography, for separation of components of a mixture, and a fast scanning mass spectrometer<sup>48</sup>, for the identification of the several components, has been applied with success; the removal of carrier gas from the gas-liquid chromatography effluent by molecular separators is, however, vital to the practical application of the technique.

A great number of compounds, organic and inorganic, have been examined by mass spectrometry. In general, when the spectrum of a pure unknown compound is obtained it can be compared with files of the mass spectra of known compounds. For this type of processing computers are commonly used, either on or off line<sup>49</sup>. When the spectrum does not compare well with the references, a more detailed study of the spectrum is necessary. The parent ion<sup>50</sup> should be recognised whenever possible before comparing the mass spectrum with others of known compounds having similar fragmentation patterns. One of the unresolved problems in this type of study is that there is no system of compiled data accepted by all workers in this field.

Some specific rules for the fragmentation of many classes of compounds<sup>51</sup> have been established, and this information is stored so that it is available through computer programmes. Two very advanced systems in the interpretation of low-resolution spectra are available: The first is the Dendral<sup>52</sup> programme developed at Stanford University. The input to the programme is the molecular formula of the molecule under consideration and the information produced is a list of all the possible structural isomers of this composition. The second system derives from an application to mass spectrometry of artificial intelligence based on learning machine theory<sup>53</sup> and is fundamentally similar to the Stanford group's approach. It differs, however, in that instead of the programmes being produced based on the available data, in this case the computer "looks" at the mass spectra and builds up its own knowledge about the nature of the mass spectra of the several types of compounds.

It was demonstrated by Aston<sup>54</sup> and developed by Beynon<sup>55</sup> for organic molecules, that differences in the nuclear packing fractions<sup>56</sup> of the elements make it possible to determine the elemental constitution of an ion provided high-resolution is available. Precise mass measurement using a mass spectrograph can be accomplished by recording

the high-resolution spectrum of the sample and reference compound on a photographic plate. The distance on the plate between ions of the sample and ions of the reference compound is measured with a travelling microscope and is related to the mass difference. To avoid such an impractical procedure Biemann<sup>57</sup> introduced a system in which measurements are made automatically and the results processed by a computer; the data are presented in the form of an "element map." Burlingame<sup>58</sup> and McLafferty<sup>59</sup> use other representations of the high-resolution data. Precise mass measurement carried out on a Nier-Johnson type instrument by the peak matching technique<sup>60</sup> is time consuming and so methods<sup>61</sup> have been developed in which the time interval between the ions is related to their mass difference and again the results are processed by a computer.

The interpretation of high-resolution data<sup>62</sup> again requires the consideration of fragmentation patterns, and computers<sup>63</sup> have been widely used to ease this interpretation. The analysis of peptides<sup>62, 64</sup> is an example of a highly successful application of computer-aided interpretation of high-resolution mass spectra.

Two major approaches towards a theory rationalising the mass spectral data and thus explaining the reactions occurring in the mass spectrometer have been developed. The first is the Quasi-Equilibrium Theory (Q.E.T.) developed by Rosenstock, Wahrhaftig and Eyring<sup>65</sup> in 1952. It assumes that:

- (i) Ionisation has taken place by a Franck-Condon transition.
- (ii) The time of residence of the ion in the source is sufficient to permit any excess electronic energy to be randomly distributed over the molecular ion.
- (iii) The energies normally employed in an electron bombardment source are such that the ions formed are distributed over a very large number of electronically excited states.
- (iv) The mass spectrum is assumed to result from a series of competing

unimolecular dissociations for which the reaction rates can be calculated from a suitable form of the absolute rate theory.

There is good agreement between the calculated and observed mass spectra of some small molecules<sup>65b)</sup> but for larger molecules the method proves to be too complex. Recently some spectral features<sup>66, 67</sup> have been explained qualitatively using the Quasi-Equilibrium Theory.

The second approach, more empirical and more easily applied, uses the same basic principles as organic solution chemistry, i.e., resonance, inductive and steric effects, stabilities of carbonium ions, etc. The formation of abundant ions in the mass spectrum was suggested by McLafferty<sup>68</sup> to depend on the relative stabilities of:

- (i) The ion and the neutral fragment.
- (ii) The bonds of the decomposing ion.
- (iii) The possibility of fragmentation through a transition state.

One of the assumptions of this approach was that of charge localisation at favoured positions in the molecule. Djerassi<sup>69</sup> and his school used this charge localisation to rationalise many mass spectral fragmentations. In contrast, Biemann<sup>70</sup> proposed a set of empirical rules, without the charge localisation principle, summarising known fragmentations and with Mandelbaum<sup>71</sup> he has shown that charge is not irreversibly localised at any particular site in the molecule.

As a consequence of the success of molecular orbital approaches in predicting the course and stereochemistry of a large number of reactions of organic neutral molecules, several authors have recently attempted to apply Molecular Orbital Theory (M.O.T.) to organic mass spectrometry. A Perturbation Molecular Orbital (P.M.O.) approach to mass spectrometric reactions is discussed by Dougherty<sup>72, 73</sup>. Despite the success of orbital symmetry rules<sup>74, 75</sup> in predicting the course of thermal and photochemical electrocyclic reactions, the applications in organic mass spectrometry are limited at present because when the molecule is ionised the shape of the molecule may be changed.

The ions which may be formed in the source of a mass spectrometer are of the following categories:

- (i) Parent or molecular ion.
- (ii) Fragment ions.
- (iii) Metastable ions.
- (iv) Rearrangement ions.
- (v) Ions formed by intermolecular processes.
- (vi) Multiply-charged ions.
- (vii) Ions formed with excess kinetic energy.
- (viii) Negative ions.

Together with these ions, neutral fragments (radicals or molecules) are formed, but not usually detected. Recently a quadrupole mass spectrometer<sup>76</sup> has been designed for convenient detection of neutral fragments formed when molecules interact with energetic electrons. It is the first four categories of ions which find most active use in conventional correlation studies. Metastable ions have been a valuable source of information to the organic mass spectroscopist. They are extremely useful in the determination of the various fragmentation pathways of an ion as well as in giving thermodynamic information about the mass spectrometric processes. McLafferty<sup>77</sup> and coworkers have applied information deriving from metastable ions to deduce ion structures and Beynon<sup>78</sup> and coworkers have used metastable data for kinetic energy studies.

Systems of instrumentation have been devised<sup>79, 80, 81</sup> to detect metastable peaks with great sensitivity. In the technique of Barber,<sup>81</sup> the Ion Kinetic Energy Spectrum (I.K.E.S.) obtained displays all the metastable peaks. To identify the metastable transitions the Ion Kinetic Energy Spectrum must be mass analysed, which requires the setting of the electrostatic and magnetic fields at values related to the masses both of the parent and the fragment ions. It is usually necessary in practice to employ both computer control of the scan and computer



processing of the data<sup>82</sup>. Recently, the study of metastable decompositions after the magnetic sector, that is, after mass analysis, has been made either using scintillation collection<sup>83a)</sup> or using an electrostatic sector for energy analysis<sup>83b),c)</sup>.

Among the methods currently used in ion structure determinations and ion decomposition studies, other than metastable ion characteristics, are: thermochemical measurements, isotopic labelling, substituent effects, ion-molecule reactions and chemical ionisation.

The calculation of heats of formation of organic ions from appearance potential data has provided evidence for the identity or non-identity of ion structures<sup>84,85</sup>. These calculations have been carried out with some recognition of the limitations imposed by the kinetic shift and excess energy terms<sup>86,87</sup>.

Hydrogen and carbon scrambling on the time scale of the mass spectrometer may be extensive in organic ions produced by electron impact. A scrambling reaction is a rearrangement in which the precursor and product ions have the same elemental composition. Such rearrangements would be expected to have tight transition states (low frequency factor) and, according to the Quasi-Equilibrium Theory, compete less effectively with other reactions at high energy<sup>67,88</sup>.

Ion decompositions and structures have been studied by the use of isotopic labelling<sup>89</sup>. In addition to deuteration there has been an increase in the use of carbon-13, nitrogen-15 and oxygen-18 labelling. However, care must be taken when using isotopes as scrambling of atoms<sup>90</sup> and isotope effects can occur.

Kinetic derivations have been attempted in order to explain mass spectral substituent effects in general and the spectra of some compounds in particular<sup>91</sup>. In some cases good correlations of substituent effects with Hammett sigma values have been found<sup>92,93,94</sup>. Chin and Harrison<sup>95</sup> confirmed that no direct information on the rate of a specific fragmentation could be obtained in this way. In many

cases the good agreement obtained shows that there is a connection between the lowering of the ionisation potentials and the power of the electron-donating substituent<sup>96</sup>.

For quantitative studies of ion-molecule reactions involving organic ions two methods have been used. The first employs medium and high pressure ion-sources in both aliphatic<sup>97, 98, 99, 100, 101</sup> and aromatic systems<sup>102, 103, 104</sup> and the second involves Ion Cyclotron Resonance (I.C.R.) spectroscopy<sup>34</sup>. This latter technique is a powerful tool for distinguishing between structural isomers of low energy organic ions.

As a particular case of high pressure source, chemical ionisation<sup>41</sup> provides spectra which are less complex than those from electron impact and the reactions can be treated in a similar way to those of solution chemistry using the Arrhenius equation and the Hammett correlations.

It can be seen from this general summary that mass spectrometry is useful in many branches of science. Of these, a number have not been considered in any detail here, including inorganic applications, chemical-physical studies, nuclear, biological, geological, environment and pollution studies, earth and cosmic science.

Bibliography (Chapter 1.)

1. E. Goldstein, Berl. Ber., 1886, 39, 691.
2. W. Wien, Ann. Physik, 1898, 65, 440.
- 3.(a) J.J. Thomson, Phil. Mag., 1911, 21, 225.
- (b) J.J. Thomson, "Rays of Positive Electricity," Longmans, Green & Co., London, 1921.
4. F.W. Aston, Phil. Mag., 1919, 38, 707.
5. A.J. Dempster, Phys. Rev., 1918, 11, 316.
6. For a description of a Faraday Cup.  
J.H. Beynon, "Mass Spectrometry and its Applications to Organic Chemistry," Amsterdam, Elsevier Publishing Co., 1960, p.200.
7. K. Biemann, 11th Ann. Conf. on Mass Spect., San Francisco, May, 1963, p.235.
8. J. Roboz, "Introduction to Mass Spectrometry, Instrumentation and Techniques, " John Wiley and Sons, New York, 1968, p.11.
9. N.F. Barber, Proc. Leeds Phil. Lit. Soc., Sci. Sect., 1933, 2, 427.
- 10.(a) W.E. Stephens and A.L. Hughes, Phys. Rev., 1934, 45, 123.
- (b) W.E. Stephens, Phys. Rev., 1934, 45, 513.
11. A.O. Nier, Rev. Sci. Instr., 1940, 11, 212.
12. Reference 6, p.9.
13. W. Bleakney, Phys. Rev., 1929, 34, 157.
- 14.(a) Allen Type - J.S. Allen, Phys. Rev., 1939, 55, 336.
- (b) Venetian blind - L.G. Smith, Rev. Sci. Instr., 1951, 22, 166.
15. Specification for MAT VARIAN CH5 (10% valley).
16. R.F.K. Herzog, Z. Physik, 1934, 89, 447.
17. J. Mattauch, Phys. Rev., 1936, 50, 617, 1089.
18. J. Mattauch and R.F.K. Herzog, Z. Physik, 1934, 89, 786.
19. E.G. Johnson and A.O. Nier, Phys. Rev., 1953, 91, 10.
20. W. Bleakney and J.A. Hipple, Jr., Phys. Rev., 1938, 53, 521.

21. K.T. Bainbridge and E.B. Jordan, Phys. Rev., 1936, 50, 282.
22. K.T. Bainbridge and E.B. Jordan, Phys. Rev., 1936, 49, 421.
23. E.G. Johnson and A.O. Nier, Phys. Rev., 1953, 91, 10.
24. H. Ewald, H. Liebl and G. Sauermann, Z. Naturforsch., 1959, 14a, 129.
25. H. Matsuda, S. Fukumoto, Y. Kuroda, M. Nojiri, Z. Naturforsch., 1966, 21a, 25.
26. H. Matsuda, S. Fukumoto, T. Matsuo, M. Nojiri, Z. Naturforsch., 1966, 21a, 1304.
27. K.I. Mayne, Repts. Progr. in Phys., 1952, 15, 24.
- 28.(a) A.E. Cameron and D.F. Eggers, Jr., Rev. Sci. Instr., 1948, 19, 605.
- (b) W.C. Wiley and I.H. McLaren, Rev. Sci. Instr., 1955, 26, 1150.
- 29.(a) W. Paul and H. Steinwedel, Z. Naturforsch., 1953, 8a, 448.
- (b) W. Paul and H. Raether, Z. Physik., 1955, 140, 262.
30. W.H. Bennett, J. Appl. Phys., 1950, 21, 143.
31. P.A. Redhead, Can. J. Phys., 1952, 30, 1.
32. J.A. Hipple, H. Sommer and H.A. Thomas, Phys. Rev., 1950, 78, 332, *ibid* 1951, 82, 697.
- 33.(a) L.G. Smith, Phys. Rev., 1951, 81, 295.
- (b) L.G. Smith, Rev. Sci. Instr., 1951, 22, 115.
34. J.D. Baldeschwieler, Science, 1968, 159, 263.
35. A.O. Nier, Rev. Sci. Instr., 1947, 18, 398.
36. A.J. Dempster, Phys. Rev., 1918, 11, 316.
- 37.(a) R.F.K. Herzog and F.P. Viehbock, Phys. Rev., 1949, 76, 855.
- (b) G.K. Wehner, Adv. Electron. and Electron Phys., 1955, 7, 239.
- 38.(a) A.J. Dempster, Proc. Amer. Phil. Soc., 1935, 75, 755.
- (b) A. Cornu in "Advances in Mass Spectrometry," Vol. IV, Ed. E. Kendrick, The Institute of Petroleum, London, 1968, p.401.

- 39.(a) F.P. Lossing and I. Tanaka, J. Chem. Phys., 1956, 25, 1031.
- (b) H.D. Beckey and F.J. Comes in "Topics in Organic Mass Spectrometry," Ed. A.L. Burlingame, Wiley-Interscience, 1970, p.1.
- 40.(a) M.G. Inghram and R. Gomer, Z. Naturforsch., 1955, 10a, 863.
- (b) Reference 39 (b).
- 41.(a) F.H. Field and M.S.B. Munson, J. Amer. Chem. Soc., 1965, 87, 3289.
- (b) J.M. Wilson in "Mass Spectrometry," Vol.1, Specialist Periodical Reports, The Chemical Society, London, 1971, p.2.
42. M.J. O'Neal and T.P. Wier, Jr., Analyt. Chem., 1951, 23, 830.
43. V.J. Caldercourt, Analyt. Chem., 1955, 27, 1670.
- 44.(a) P. de Mayo and R.I. Reed, Chem. and Ind., 1956, 1481.
- (b) J.H. Beynon, R.A. Saunders and A.E. Williams, Appl. Spect. 1963, 17, 63.
45. H. Hoover and H.W. Washburn, Amer. Inst. Min. Met. Engineers, 1940, Tech. Publ. No.1205, Calif. Oil World, 1941, 34, 21.
- 46.(a) H.W. Washburn, H.F. Wiley, S.M. Rock and C.E. Berry, Ind. Eng. Chem. Analyt. Ed., 1945, 17, 74.
- (b) A.K. Brewer and V.H. Dibeler, J. Res. N.B.S., 1945, 35, 125.
47. L. Fraser Monteiro and R.I. Reed, Int. J. Mass Spect. and Ion Phys., 1969, 2, 265.
- 48.(a) J.C. Holmes and F.A. Morrell, Appl. Spect., 1957, 11, 86.
- (b) R.S. Gohlke, Analyt. Chem., 1959, 31, 535.
- (c) C.J.W. Brooks in Reference 41 (b) p.288.
- 49.(a) F.W. McLafferty in "Advances in Mass Spectrometry," Vol.V, Ed. A. Quale, The Institute of Petroleum, 1971, p.589.
- (b) S.D. Ward in Reference 41 b) p.253.
50. J.H. Beynon in Reference 6, p.307.
51. For compilation of these rules,  
H. Budzikiewicz, C. Djerassi and D. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, 1967.

52. J. Lederberg, G.L. Sutherland, B.G. Buchanan, E.A. Feigenbaum, A.V. Robertson, A.M. Duffield and C. Djerassi, J. Amer. Chem. Soc., 1969, 91, 2973.
- 53.(a) N.J. Nilsson, "Learning Machines," McGraw Hill, Inc., New York, 1965.  
(b) P.C. Jurs, B.R. Kowalski and T.L. Isenhour, Analyt. Chem., 1969, 41, 21.
54. F.W. Aston, "Isotopes," Edward Arnold and Co., London, 1942.
55. J.H. Beynon in "Advances in Mass Spectrometry," Vol.I, Ed. J.D. Waldron, The Institute of Petroleum, London, 1959, p.328.
56. F.W. Aston, "Mass Spectra and Isotopes," Edward Arnold and Co., London, 1942, p.80.
- 57.(a) D. Desiderio and K. Biemann, 12th Ann. Conf. on Mass Spect., Montreal, June, 1964, p.433.  
(b) C. Cone, P. Fennessey, R. Hites, N. Marcuso and K. Biemann, 15th Ann. Conf. on Mass Spect., Denver, May, 1967, p.114.
58. A.L. Burlingame and D.H. Smith, Tetrahedron, 1968, 24, 5749.
59. R.Venkataraman and F.W. McLafferty, Analyt. Chem., 1967, 39, 278.
60. K.S. Quisenberry, T.T. Scolman and A.O. Nier, Phys. Rev., 1956, 102, 1071.
61. W.J. McMurray, B.N. Green and S.R. Lipsky, Analyt. Chem., 1966, 38, 1194.
62. R.K. Biemann in Reference 39 (b) p.185.
- 63.(a) K. Biemann and P.V. Fennessey, Chimia, 1967, 21, 226.  
(b) R. Venkataraman, F.W. McLafferty and G.E. Van Lear, Org. Mass Spect., 1969, 2, 1.  
(c) Y. Ishida, Y. Kudo, M. Sakamoto, H. Abe, S. Sasaki in "Recent Developments in Mass Spectroscopy," Proc. Int. Conf. Mass Spectroscopy, Ed. K. Ogata and T. Hayakawa, University of Tokyo Press, Kyoto, 1970, p.1286.
64. R.G. Cooks and G.S. Johnson in Reference 41 (b) p.139.

- 65.(a) H.M. Rosenstock, M.B. Wallenstein, A.L. Wahrhaftig and H. Eyring, Proc. Nat. Acad. Sci. U.S.A., 1952, 38, 667.
- (b) H.M. Rosenstock and M. Krauss in "Advances in Mass Spectrometry," Vol.II, Ed. R.M. Elliot, Pergamon Press, 1963, p.251.
66. D.H. Williams in Reference 49 (a) p.569.
67. I. Howe in Reference 41 (b) p.31.
68. F.W. McLafferty in "Mass Spectrometry of Organic Ions," Ed. F.W. McLafferty, Academic Press., New York, 1962, Chapter 7.
69. H. Budzikiewicz, C. Djerassi and D.H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day Inc., San Francisco, 1967, p.9.
70. K. Biemann, "Mass Spectrometry," McGraw-Hill, New York, 1962.
71. A Mandelbaum and K. Biemann, J. Amer. Chem. Soc., 1968, 90, 2975.
72. R.C. Dougherty, J. Amer. Chem. Soc., 1968, 90, 5780.
73. R.C. Dougherty in Reference 72, p.5788.
74. R. Hoffmann and R.B. Woodward, Accounts Chem. Res., 1968, 1, 17.
75. R.B. Woodward and R. Hoffmann, Angew. Chem., Internat. Ed., 1969, 8, 781.
76. J.R. Reeher and H.J. Svec in "Advances in Mass Spectrometry," Vol.VI, Ed. A.R. West, The Institute of Petroleum, London, 1974, p.509.
77. F.W. McLafferty, T. Wachs and W.T. Pike in Reference 38 (b), p.153.
78. J.H. Beynon, Analyt. Chem., 1970, 42, 97A (No.1).
- 79.(a) K.R. Jennings, J. Chem. Phys., 1965, 43, 4176.
- (b) J.H. Futtrell, K.R. Ryan and L.W. Siek, J. Chem. Phys., 1965, 43, 1832.
80. M.R. Daly, A. McCormick and R.E. Powell, Rev. Sci. Instr., 1968, 39, 1163.

- 81.(a) M. Barber and R.M. Elliott, 12th Ann. Conf. on Mass Spect., Montreal, June, 1964, p.150.
- (b) H.W. Major, Docket No.D-1185, U.S. Patent Office, Washington, D.C., 1968.
82. T.W. Shannon, T.E. Mead, C.G. Warner and F.W. McLafferty, *Analyt. Chem.*, 1967, 39, 1748.
- 83.(a) N.R. Daly, A. McCormick and R.E. Powell in Reference 49 (a) p.300.
- (b) K.H. Maurer, C. Brunee, G. Kappus, K. Habfast, U. Schröder and P. Schulze, 19th Ann. Conf. on Mass Spect., Atlanta, May, 1971.
- (c) T. Wachs, P.F. Bente, III and F.W. McLafferty, *Int. J. Mass Spect. and Ion Phys.*, 1972, 2, 333.
84. R.G. Cooks, I. Howe and D.H. Williams, *Org. Mass Spect.*, 1969, 2, 137.
85. A.G. Harrison in Reference 39 (b)
86. R.G. Gillis, G.J. Long, A.G. Moritz, and J.L. Occolowitz, *Org. Mass Spect.*, 1968, 1, 527.
87. D.H. Williams, R.G. Cooks, and I. Howe, *J. Amer. Chem. Soc.*, 1968, 90, 6759.
- 88.(a) W.A. Chupka, *J. Chem. Phys.*, 1959, 30, 191.
- (b) D.H. Williams and R.G. Cooks, *Chem. Comm.*, 1968, 1, 663.
- (c) R.G. Cooks, *Org. Mass Spect.*, 1969, 2, 481.
- 89.(a) M.F. Grostic and K.L. Rinehart, Jr., in "Mass Spectrometry Techniques and Applications," Ed. G.W.A. Milne, Wiley-Interscience, 1971, p.217.
- (b) I. Howe, in Reference 41 (b) p.53.
90. W.G. Cole, D.H. Williams and A.N. Yeo, *J. Chem. Soc.(B)*, 1968, 1284.



91. N. Einoef and B. Munson, Org. Mass Spect., 1971, 5, 397.
92. F.W. McLafferty in Reference 39 (b)
93. F.W. McLafferty and M.M. Bursey, J. Org. Chem., 1968, 33,  
124.
94. F.W. McLafferty, Chem. Comm., 1968, 1, 254.
95. M.S. Chin and A.G. Harrison, Org. Mass Spect., 1969, 2, 1073.
96. A.N.H. Yeo and D.H. Williams, J. Chem. Soc. (C), 1968, 2666.
97. H. Pritchard, J.C.J. Thynne, and A.G. Harrison, Can. J. Chem.,  
1968, 46, 2141.
98. G.P. Nagy, J.C.J. Thynne and A.G. Harrison, Can. J. Chem.,  
1968, 46, 3609.
99. H. Pritchard and A.G. Harrison, J. Chem. Phys., 1968, 48, 5623.
100. J.A. Herman, J.J. Myher and A.G. Harrison, Can. J. Chem., 1969,  
47, 647.
101. J.A. Herman and A.G. Harrison, Can. J. Chem., 1969, 47, 957.
102. S. Wexler and R.P. Clow, J. Amer. Chem. Soc., 1968, 90, 3940.
103. F.H. Field, P. Hamlet and W.F. Libby, J. Amer. Chem. Soc.,  
1969, 91, 2839.
104. C. Lifshitz and B.G. Reuben, J. Chem. Phys., 1969, 50, 951.

## Chapter 2.

The determination of the masses of the ions by  
spline-fit interpolation

2.1. Introduction

The use of the mass spectrometer for the qualitative identification of organic compounds has been demonstrated by Beynon<sup>1,2</sup>, and McLafferty<sup>3</sup>, who have shown that semi-empirical rules can be formulated correlating the mass spectrum of a compound with its molecular structure. With the aid of such rules, much useful work can be done, but difficulties arise in the interpretation of the mass spectrum if several different kinds of atoms are present in the molecule, since it is then possible to postulate several alternative atomic groupings at a particular mass number. Although the accurate measurement of mass by mass spectrometry and spectrography has been carried out since the days of Aston, its application to organic chemical analysis as a routine technique is recent. Experiments carried out in 1954 by Beynon<sup>1</sup>, using a single-focusing mass spectrometer of resolving power 200, confirmed that accurate mass measurement of parent molecular ions enabled the empirical formula of an unknown compound to be deduced.

In 1959, Beynon<sup>4,5</sup> pointed out the importance of the use of double-focusing, high-resolution mass spectrometry, for the determination of the precise mass of the ions produced with an accuracy sufficient to differentiate amongst various elemental combinations of the same nominal mass. In this early work an MS8 mass spectrometer having the Nier-Johnson geometry was used.

In the double-focusing instruments accurate mass measurements on fragment ions are made possible, unaffected by any kinetic energy of formation of these ions. The greater stability of the electronic

circuits which are necessary at the higher resolving power, together with the increased sharpness of the mass peaks resulting from this resolving power, make all mass measurements more accurate and easier to perform than on single-focusing instruments<sup>5</sup>.

However, Kerr<sup>6</sup> and Duckworth<sup>7,8</sup>, using a 180 degree mass spectrometer, have shown that a double-focusing instrument is not essential for very accurate mass measurements provided that there is no possibility of any ions being formed with kinetic energy.

In both cases, mass measurements with single and double-focusing instruments should be carried out at the highest possible voltages so as to minimise the effects of stray potentials and initial kinetic energy of formation of fragment ions<sup>4</sup>.

Since the pioneering work of Beynon the technique of high-resolution mass spectrometry has been a subject of great interest to mass spectrometrists and organic chemists.

Most early work concerned with the study of the high-resolution mass spectra of organic compounds employed one of the following two techniques to determine the mass of an ion with an accuracy of one part in  $10^5$  to  $10^6$ :

(a) Electronic recording of a part or of the entire spectrum and calculation of the mass of the unknown species from the position of a peak of known mass recorded on the chart. Either a mass quadrant<sup>9</sup> or a transparent Perspex scale<sup>9</sup> was used to carry out the mass determination.

(b) Measurement of the ratio of accelerating potentials necessary to bring first the peak of unknown mass and then the peak of known mass into register at the collector slit. The most sophisticated method of this ratio measurement is the "peak-matching" technique of Nier<sup>10,11</sup>, originally designed for doublet measurement in connection with accurate atomic mass determination and later applied by Beynon<sup>4</sup>

to molecular formula determination. In this application it is considered advisable to use reference masses within 10% of the unknown mass<sup>12,13</sup>. However, Fales and coworkers<sup>14</sup> have reported measurements of peaks within 10 ppm using ratios from 1.0 - 2.0 in mass.

Wolstenholme<sup>15</sup> has developed an extension to the accelerating voltage ratio method for precise mass measurement which allows up to fifty peaks to be determined in one hour; diminished accuracy, however, results.

Although the methods described by Beynon have been responsible for valuable developments in the application of mass spectrometry to the structural elucidation of organic compounds, they possess certain inherent disadvantages.

The peak matching technique is time consuming and requires a judgment of which peaks are to be measured while the sample is still in the instrument. A relatively large sample and additional instrument time is usually required and the data are not produced in a form readily amenable to treatment by computer techniques. Also there have been very few cases in which it has proved possible to record the entire mass spectrum of a compound with high resolution. The method is limited to small molecules because of the slowness of recording with high resolving power<sup>16</sup>.

Biemann and coworkers<sup>17,18</sup> have argued that to realise the full potential of high-resolution mass spectrometry it is necessary to measure the elemental composition of all masses observed and to use all these data in the interpretation of the spectra, just as in conventional single-focusing mass spectrometry the entire spectrum is scanned, rather than selected regions thereof. For this reason, they have developed techniques which make possible the determination of the accurate masses of all ions produced on electron impact on an organic compound of molecular weight up to one thousand. A routine, semi-

automatic procedure has been established by means of which, using a Mattauch-Herzog type double-focusing instrument, the CEC 21-110 spectrometer, a spectrum is obtained on a photographic plate. To produce lines of known mass, necessary for the calculation of the exact masses of the ions derived from the sample, a calibration compound of very different elemental composition to the sample is added simultaneously. This procedure results in a composite mass spectrum consisting of a set of lines of known mass dispersed amongst a set of lines of unknown mass which are to be measured. The line intensities are measured using a densitometer, after which the line positions are measured using a digital comparator which gives as its output a punched card record of the line positions and intensities. These cards are fed to a computer which calculates the exact mass of each of the unknown ions in the spectrum<sup>19</sup>. The arithmetic involved in the mass calculation is very simple, namely, the relationship of the distance on the plate, from an arbitrary zero point, to the square root of the mass<sup>20,21</sup>. The elemental composition corresponding to a given mass, which could be found by hand calculation, (systematic addition or short-cut methods<sup>22,23</sup>) or by searching available tables<sup>24</sup>, is again usually calculated by computer<sup>19</sup>. The data are presented in the form of the so-called "element map"<sup>20,25</sup> which summarises the features of the spectrum and also presents them in a much more condensed form.

The methods of Biemann have greatly influenced research work employing computer techniques in the acquisition and processing of data in general and mass measurements in particular.

Basically there are two methods of computerised data acquisition and processing for mass measurement. They differ in the recording system employed, the choice lying between photographic or electrical methods of recording.

Photographic recording is normally effected by one of two

techniques. In the first, the comparator is on-line to the computer; alternatively there is some form of intermediate storage, which may be paper tape, magnetic tape<sup>26</sup> or punched cards, between the comparator and the computer.

In the Biemann off-line system the time required for the measurement of line positions was one or two hours. Burlingame<sup>27</sup> and Olsen<sup>28</sup> reduced the time required for this measurement by employing a commercial recording microphotometer (Jarrell-Ash, Model 23-500). This instrument yields line-position measurements to the nearest micron, compared to 0.5 micron for the Biemann system. In this system the accurate mass is calculated from a quadratic interpolation using fluorocarbon mass calibration<sup>27</sup>. The precision of mass measurement is about the same as for the method of Biemann, namely one millimass unit. Results obtained by both techniques have demonstrated that the punched card or magnetic tape output of these measuring systems can be used directly for the computer calculation of exact masses and the preparation of element maps.

In the fully automatic off-line system described by McLafferty and coworkers<sup>29</sup>, the transmittance values are measured at 0.25 micron intervals across each ion band and a special comparator-densitometer yields data describing the ion distribution in accurate detail. Computer calculations using these data not only provide accurate masses but can also separate overlapping ion bands. Thus this system makes possible a substantial increase in both the mass-measuring accuracy and resolving power obtainable from the spectral data of high-resolution instruments, while greatly reducing the time and manpower required to obtain an element map from a sample. Peak positions are converted to masses by employing the square root relationship between distance and mass, using the exact masses arising from the calibration compound perfluorokerosene as reference points throughout the spectrum. The

interpolation and extrapolation procedure used to evaluate the exact masses of the ions in the spectrum of the sample is similar to that described by Biemann<sup>19</sup>, except that increased accuracy appears possible by the use of higher order polynomials for interpolation. Possible elemental compositions fitting the observed masses of the sample lines within a predetermined tolerance are then computed using an iterative procedure.

The system described above has been modified by Tunnicliff and Wadsworth<sup>31</sup> to incorporate more sophisticated and efficient automatic recording. An improvement in performance was reported.

Biemann and others<sup>32,33</sup> have demonstrated a system designed to obtain data with an on-line computer located in the laboratory.

In the on-line system of Desiderio and Mead<sup>34,35</sup>, an automatic densitometer-comparator which reads transmission values every 0.5 micron is combined with a medium size, high-speed, time-shared digital computer connected via a direct cabling system to transmit high-resolution mass spectral photoplate data. Using a Fortran programme, the computer reads the peaks into a memory, calculates peak centres and areas, resolves unresolved doublets by a non-linear least squares procedure, calculates masses, elemental compositions, and prints an element map and a "low resolution spectrum" with a list of all elemental compositions found. The methods of acquiring the data and reducing them are different in the two on-line processes, but in both Biemann's system and Desiderio's system there is no intermittent storage of data during the acquisition step.

The photographic techniques have the advantage that they give a permanent record, allow the data processing to be independent of the mass spectrometer, and require no preinterpretation before the final output is received<sup>30</sup>. However, they have shortcomings which include the variabilities of exposure times and photographic processing and

the sensitivity of the emulsion to damage.

As regards electrically recorded spectra, Merritt, Green and coworkers<sup>36,37</sup> and McMurray and his colleagues<sup>38,39</sup> have demonstrated that direct analogue recording of a high-resolution mass spectrum on magnetic tape is possible in ten seconds to a few minutes, according to resolving power. Automatic conversion of these data to digital form makes possible computer calculation of exact masses and the preparation of element maps<sup>38</sup>. Under these circumstances the masses of all fragment ions present in a spectrum can be measured to an average accuracy better than 10 ppm. An extrapolation technique similar to that described previously<sup>19</sup> but based on an exponential mass-time relationship is employed.

The results presented by these authors suggest that fast scanning and electrical recording of high-resolution mass spectra is feasible<sup>40</sup>.

The sensitivity and accuracy of mass measurement attainable appear adequate to permit the use of a double-focusing magnetic scanning mass spectrometer for the analysis of gas chromatographic effluents and other samples if the quantity of material available is of the order of  $10^{-7}$  gram per second<sup>36</sup>.

The basic configurations of the mass spectrometer, computer and analogue-to-digital converter are as in the photographic technique on and off-line systems.

In the on-line system A, the mass spectrometer, the analogue-to-digital converter and computer are directly connected together and can "communicate" with each other.

In the off-line scheme there are two possible arrangements: in one of the systems, B, the spectrum is stored in analogue form, while in the other, C, the spectrum is digitised and then stored.

A number of workers have described systems employing on-line



computers utilising analogue-to-digital converters for direct digitisation of multiplier-amplifier output and data acquisition during exponential magnetic scans using AE I MS9 mass spectrometers.

Bowen and coworkers<sup>41,42</sup> have used a system of type A consisting of an AE I MS9 mass spectrometer and an Argus 300 computer. The output of the double-focusing mass spectrometer is fed to an analogue-to-digital converter. The digital output of the converter is presented to a digital comparator which is necessary to reduce the volume of data which is finally presented to the computer for analysis.

Several methods of using the reference masses to determine the sample masses, assuming an exponential scan-law, were investigated by these workers. Four consecutive high-mass reference peaks of perfluorokerosene having been identified, an equation of the form:

$$M = M_0 \exp ( a + bt^2 + ct^3 )$$

was generated, where  $M$  and  $M_0$  are masses of the ions,  $t$  is time in the scan, and  $a$ ,  $b$ , and  $c$  are constants. The values of the constants were determined by the use of the known masses and times of the four reference peaks. The equation was then used to extrapolate downwards in mass to the next reference peak, and when this was identified within a given tolerance, the equation was updated using the new reference peak and discarding the first one. All reference peaks down the spectrum were identified by this extrapolation procedure, and using these reference peaks the masses of all the sample peaks were determined by interpolation. Equations of the form  $M = f(t)$  which represented the mass versus time curve passing through one or more reference peaks on either side of the sample peak to be identified were generated. It was shown that the use of four reference peaks for the interpolation procedure was superior to the use of 2, 3, 6, 8 or 10 peaks.

A second method studied used a least-squares fit to the reference peaks rather than a precise fit, and it was found that a worthwhile

improvement in accuracy could be obtained.

The standard deviations for mass measurements using the best precise fitting and linear-regression fitting methods on spectra of perfluorokerosene, which were recorded at a resolution of 10,000, and a scan rate of 10 s per decade, were 4.9 ppm and 4.3 ppm respectively.

McMurray and coworkers<sup>43,44</sup>, and Merritt and coworkers<sup>45</sup> also discussed systems employing on-line computers and reported a system which is a hybrid of types A and B. For a scan speed of 40 s per decade at a resolution of 10,000, spectra could be recorded on-line. For faster scan rates, intermediate recording on an analogue tape recorder was employed. The average error reported by McMurray and coworkers was 4 ppm, while in the work of Merritt and coworkers the average error was 30 ppm.

Burlingame and Olsen<sup>46,47</sup> have described a technique in which direct digitisation of multiplier-amplifier output from a CEC 21-110B mass spectrometer and on-line data transfer to a high-speed digital computer has been employed. This system differs from others in that a high precision magnetic scan, quadratic in mass, was utilised as a scanning function instead of the conventional exponential scan. Results obtained by the same authors employing the Nier-Johnson geometry coupled to a computer demonstrate accuracy better than 0.5 ppm<sup>48</sup>.

A sophisticated system which is basically of type C has been described also by Burlingame<sup>49</sup>. Two types of scanning mass spectrometers were used; an AEI MS9, which has Nier-Johnson geometry and a magnetic scan giving an exponential mass versus time relationship, and a CEC 21-110B, which has Mattauch-Herzog geometry and a mass proportional to time-squared scan law. In this off-line arrangement, the feasibility of a rapid check on performance (possible with any on-line arrangement) confers major advantages over many other, less expensive, off-line systems. The data from the mass

spectrometer of Mattauch-Herzog geometry<sup>49</sup> have been processed using similar interpolation procedures to those previously described. For this system, the linear magnet-scan function gave a mass proportional to time-squared scan law. The perfluorokerosene reference peaks were extrapolated from low to high mass using a three-term polynomial of the form  $M = A + Bt + Ct^2$ . The scan was found to be very reproducible and it was considered that the reference peaks could be identified by their times rather than by extrapolation procedures. The accuracy of mass measurement was found to be comparable with that of a system following an exponential scan law<sup>49</sup>.

A modification to this system has subsequently been described in which there is an increase in the maximum digitisation rate<sup>50</sup>. The results obtained indicate that curve-fitting to the reference peaks using least-square methods can give improved accuracy of mass measurement. In this case the use of seven calibration points gave the optimum results. Work by Bowen<sup>42</sup> supports these conclusions.

The interpolation procedures used to determine the masses of non-reference peaks described thus far have been carried a stage further by Aczel and coworkers<sup>51,52</sup>. A Lagrangian interpolation was first carried out for all peaks, and elemental formulae were determined from the precise masses only for sample peaks close to those of the reference compound. Under these circumstances the error in mass measurement was expected to be minimal. The remaining elemental formulae were calculated using identified sample peaks as new references for sample peaks within two integer mass units. This process was repeated until the whole of the mass range had been covered. The method was applicable, however, only because of the nature of the spectra of the petroleum mixtures being studied. As a result of the use of this technique the proportion of correctly identified peaks was increased from 80% to 92 - 98%. This automatic

data acquisition system has been applied with low ionising voltages and so the reference compounds used are different<sup>53</sup> from the conventional perfluorokerosene and heptacosafuorotributylamine. The reference standards used<sup>53</sup> consist of a blend of halogenated aromatics such as pyrrole, fluorobenzene, chlorobenzene, bromonaphthalene, iodochlorobenzene and perfluorodiphenyl.

The electrical recording of spectra provides less sensitivity than photographic recording, but electrical signals are more amenable to automatic digitisation either by special purpose data acquisition systems or by real-time computers equipped with an analogue-to-digital conversion capability<sup>45</sup>.

The progress in the development of systems for the acquisition and reduction as well as processing of data from mass spectrometers has been considerable in the last six years.

Reasonably priced computer systems are now available with the speed and capacity necessary to produce reduced data shortly after the scan is completed.<sup>54</sup>

A number of successful automated systems for measurement of photoplates from Mattauch-Herzog type instruments are in routine use<sup>55,56,29,31,34,57</sup>. The integrating nature of photoplate recording is specially useful for "element mapping"<sup>56</sup> of microgram samples of high molecular weight materials; mass-measuring accuracy of 0.5 millimass units and resolution of 60,000 have been achieved<sup>58</sup>. Some additional improvements may be possible in such systems, such as the use of grainless photoplates.

For on-line data systems, the continued improvement in computer techniques and the substantial reductions in equipment prices make such systems very promising for high-resolution mass spectrometry. Computer multi-scan averaging techniques can improve mass-measuring accuracy<sup>59,60</sup>. The day-to-day usefulness of an on-line computer

system is also dependent on the degree to which it provides a rapid, convenient and reliable communicating link between the researcher and his equipment, the high-resolution system ideally being as fully automatic as possible.

Larger system configurations using time-shared computers have still to be assigned to one or other of the basic classes of configuration described previously.

A detailed examination of sources of error in high-resolution data acquisition systems has been presented by McLafferty and coworkers<sup>61</sup> and Smith and coworkers<sup>62</sup>. In addition, a method<sup>63</sup> for improving the signal-to-noise ratio in mass spectrometry and therefore improving the accuracy of measurement of mass has been described.

Precise mass measurements for peaks greater than  $m/e$  1000 and a double exposure method using a Mattauch-Herzog geometry double-focusing mass spectrometer have been described<sup>57</sup>.

Each year increasingly sophisticated systems using computers for data acquisition and processing in mass spectrometry are presented, and yet the mathematical procedures employed to transform peak positions or times into mass are basically unchanged.

## 2.2. Theory

The basic problem in curve fitting can be described as follows<sup>64</sup>. A set of measured values of a quantity  $x$  is obtained, and likewise an associated set of measured values of another quantity  $y$ . It is necessary to find some functional relation between  $x$  and  $y$ ,

$$y = f(x),$$

which is satisfied by the sets of measured values  $(x_1, y_1)$ ,  $(x_2, y_2)$ , etc., and which will allow the inference of reasonable values of  $y$  corresponding to values of  $x$  intermediate between the measured values.

In this work a new method of curve-fitting and subsequent interpolation has been attempted. The points are plotted, and a smooth curve is drawn through these points using a draughtsman's spline in such a way that the curve, its slope and its curvature are continuous functions. Interpolation is then readily performed by reading points off the smooth curve thus generated.

Let the given set of points be  $(x_1, y_1)$ , ...,  $(x_m, y_m)$ , arranged in order of increasing values of  $x$ . The spline-fit is accomplished by connecting each pair of adjacent points with a section of a third-degree polynomial, matching up the sections so that the first and second derivatives are continuous at each point<sup>64</sup>.

Let  $Z_1, Z_2, \dots, Z_m$  be the values of the second derivative at the points; then between points  $(x_k, y_k)$  and  $(x_{k+1}, y_{k+1})$  the second derivative has the value:

$$y'' = Z_k \frac{x_{k+1} - x}{d_k} + Z_{k+1} \frac{x - x_k}{d_k} \quad (1)$$

where  $d_k = x_{k+1} - x_k$ .

Integrating, the first derivative is of the form

$$y' = -Z_k \left[ \frac{(x_{k+1} - x)^2}{2d_k} \right] + Z_{k+1} \left[ \frac{(x - x_k)^2}{2d_k} \right] + c_1 \quad (2)$$

where  $c_1$  is a constant of integration. Integrating again, the equation

of the curve is obtained as

$$y = Z_k \left[ (x_{k+1} - x)^3 / 6d_k \right] + Z_{k+1} \left[ (x - x_k)^3 / 6d_k \right] + c_1 x + c_2 \quad (3)$$

where  $c_2$  is a constant of integration. The constants  $c_1$  and  $c_2$  can be evaluated from the fact that the curve passes through  $(x_k, y_k)$  and  $(x_{k+1}, y_{k+1})$ . Thus, since

$$y_k = (Z_k d_k^2 / 6) + c_1 x_k + c_2 \quad (4)$$

and

$$y_{k+1} = (Z_{k+1} d_k^2 / 6) + c_1 x_{k+1} + c_2 \quad (5)$$

it follows that

$$c_1 = [(y_{k+1} - y_k) / d_k] - [(Z_{k+1} - Z_k) d_k / 6] \quad (6)$$

and

$$c_2 = [(y_k x_{k+1} - y_{k+1} x_k) / d_k] - [(Z_k x_{k+1} - Z_{k+1} x_k) d_k / 6]. \quad (7)$$

Substituting these values in equation (3), the following equation for the curve is obtained.

$$\begin{aligned} y = & \left[ Z_k (x_{k+1} - x)^3 / 6d_k \right] + \left[ Z_{k+1} (x - x_k)^3 / 6d_k \right] \\ & + \left[ (x_{k+1} - x) (y_k / d_k - Z_k d_k / 6) \right] \\ & + \left[ (x - x_k) (y_{k+1} / d_k - Z_{k+1} d_k / 6) \right]. \end{aligned} \quad (8)$$

In this equation all quantities are known with the exception of  $Z_k$  and  $Z_{k+1}$ , the values of the second derivative at the end points of the interval. One condition which helps in the determination of these values is that the slope at  $(x_k, y_k)$  as determined from equation (2) must be the same as that determined by the corresponding formula for the interval  $(x_{k-1}, y_{k-1})$  to  $(x_k, y_k)$ . When the value of  $c_1$  from equation (6) is used in equation (2), the equation becomes:

$$\begin{aligned} y' = & - \left[ Z_k (x_{k+1} - x)^2 / 2d_k \right] + \left[ Z_{k+1} (x - x_k)^2 / 2d_k \right] + \\ & + \left[ (y_{k+1} - y_k) / d_k \right] - \left[ (Z_{k+1} - Z_k) d_k / 6 \right]. \end{aligned} \quad (9)$$

At the point  $(x_k, y_k)$ , these relations give

$$\begin{aligned}
 y_k' &= (-z_k d_k / 2) + [(y_{k+1} - y_k) / d_k] - [(z_{k+1} - z_k) d_k / 6] \\
 &= (z_k d_{k-1} / 2) + [(y_k - y_{k-1}) / d_{k-1}] - [(z_k - z_{k-1}) d_{k-1} / 6]. \quad (10)
 \end{aligned}$$

Collecting the unknowns  $z_{k-1}$ ,  $z_k$ , and  $z_{k+1}$  on one side of the equation,

$$\begin{aligned}
 z_{k-1} (d_{k-1} / 6) + z_k [(d_{k-1} + d_k) / 3] + z_{k+1} (d_k / 6) \\
 = [(y_{k+1} - y_k) / d_k] - [(y_k - y_{k-1}) / d_{k-1}]. \quad (11)
 \end{aligned}$$

An equation of this form is obtained for each of the internal points, that is,  $k = 2, 3, \dots, m-1$ , giving  $m-2$  equations in the  $m$  unknowns  $z_1, z_2, \dots, z_m$ . Two more conditions must therefore be specified in order to determine these quantities absolutely. It is usual to place additional conditions on  $z_1$  and  $z_m$ , the values of the second derivative at the end points. There are several reasonable assumptions which may be attached to these values, and the particular choice will influence the shape of the fit, especially near the end points. One of the assumptions is to consider the third derivative to be continuous at  $(x_2, y_2)$  and at  $(x_{m-1}, y_{m-1})$ . From equation (1) the third derivative becomes

$$y''' = -z_k / d_k + z_{k+1} / d_k. \quad (12)$$

Equating values for  $k = 1$  and  $k = 2$ ,

$$-z_1 / d_1 + z_2 / d_1 = -z_2 / d_2 + z_3 / d_2 \quad (13)$$

or

$$-z_1 / d_1 + z_2 (1/d_1 + 1/d_2) - z_3 / d_2 = 0. \quad (14)$$

In like manner, equating values for  $k = m - 2$  and  $k = m - 1$ ,

$$-z_{m-2} / d_{m-2} + z_{m-1} / d_{m-2} = -z_{m-1} / d_{m-1} + z_m / d_{m-1}$$

or

$$-z_{m-2} / d_{m-2} + z_{m-1} (1/d_{m-2} + 1/d_{m-1}) - z_m / d_{m-1} = 0. \quad (15)$$

Equations (14) and (15), along with equations of type (11), constitute  $m$  equations in  $m$  unknowns for the quantities  $z_1, z_2, \dots, z_m$ . When these



equations are solved and the  $Z_k$  values determined, the spline-fit interpolation in the table of values  $(x_1, y_1), (x_2, y_2) \dots, (x_m, y_m)$  consists of determining which two points  $(x_k, y_k)$  and  $(x_{k+1}, y_{k+1})$  enclose each given value of  $x$ . The corresponding value of  $y$  can then be found using the equation:

$$y = c_{1,k}(x_{k+1} - x)^3 + c_{2,k}(x - x_k)^3 + c_{3,k}(x_{k+1} - x) + c_{4,k}(x - x_k) \quad (16)$$

where the constants  $c_{1,k}$ ,  $c_{2,k}$ ,  $c_{3,k}$  and  $c_{4,k}$  have all been previously computed and stored.

The spline-fit interpolation method has been applied to the determination of the exact masses of the ions in the mass spectrum. In this case the variable  $x$  is the distance of the centre of each peak from a reference point; the variable  $y$  is the exact mass of each ion. Five peaks have been chosen in the spectrum as reference peaks, this number being the minimum necessary to define the curve. Their exact masses and distances are known and a computer programme constructs the spline on these variables. The interpolation is carried out by introducing the distances corresponding to the unknown peaks in the same Fortran programme which is able to make the interpolation. The one Fortran programme therefore enables the entire operation to be carried out and the output is the exact masses of the unknown peaks. On pages 36, 37 and 38 the main Fortran programme\* is set out, together with the subroutines 'splico' and 'spline' for, respectively, the calculation of the values of the constants  $c_{k,k}$  and the subsequent spline-fit interpolation in the table of five values.

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\* The American spelling is used when naming the programmes while the English spelling is used in the text.

FORTRAN IV G LEVEL 21

MAIN

```

C MAIN PROGRAM
REAL * 8 X,Y,XINT
DIMENSION X(5),Y(5),C(4,5)
400 READ(5,100)(X(I),Y(I),I=1,5)
100 FORMAT(F10.5,1X,F9.5)
WRITE(6,103)(X(I),Y(I),I=1,5)
103 FORMAT(/1X,F10.5,4X,F9.5/)
READ(5,102)M
102 FORMAT(I6)
WRITE(6,102)M
CALL SPLICO(X,Y,M,C)
MM=M-1
WRITE(6,101)((C(I,K),K=1,MM),I=1,4)
101 FORMAT(4(2X,E12.4))
WRITE(6,200)
300 READ(5,201)XINT
201 FORMAT(F9.5)
CALL SPLINE(X,Y,M,C,XINT,YINT)
WRITE(6,103)XINT,YINT
200 FORMAT(/10X,'FINAL RESULTS'////)
READ(5,204)ISTOP
204 FORMAT(I1)
IF(ISTOP.EQ.1) GO TO 300
IF(ISTOP.EQ.2) GO TO 400
CALL EXIT
END

```

```

SUBROUTINE SPLICO (X,Y,M,C)
REAL *8 X,Y
DIMENSION X(5),Y(5),D(5),P(5),E(5),C(4,5),A(5,3),B(5),Z(5)
MM=M-1
DO 2 K=1,MM
D(K)=X(K+1)-X(K)
P(K)=D(K)/6
2 E(K)=(Y(K+1)-Y(K))/D(K)
DO 3 K=2,MM
3 B(K)=E(K)-E(K-1)
A(1,2)= -1.-D(1)/D(2)
A(1,3)=D(1)/D(2)
A(2,3)=P(2)-P(1)*A(1,3)
A(2,2)=2.* (P(1)+P(2))-P(1)*A(1,2)
A(2,3)=A(2,3)/A(2,2)
B(2)=B(2)/A(2,2)
DO 4 K=3,MM
A(K,2)=2.* ( P(K-1)+P(K))-P(K-1)*A(K-1,3)
B(K)=B(K)-P(K-1)*B(K-1)
A(K,3)=P(K)/A(K,2)
4 B(K)=B(K)/A(K,2)
Q=D(M-2)/D(M-1)
A(M,1)=1.+Q+A(M-2,3)
A(M,2)= -Q-A(M,1)*A(M-1,3)
B(M)=B(M-2)-A(M,1)*B(M-1)
Z(M)=B(M)/A(M,2)
MN=M-2
DO 6 I=1, MN
K=M-I
6 Z(K)=B(K)-A(K,3)*Z(K+1)
Z(1)= -A(1,2)*Z(2)-A(1,3)*Z(3)
DO 7 K=1,MM
Q=1./(6.*D(K))
C(1,K)=Z(K)*Q
C(2,K)=Z(K+1)*Q
C(3,K)=Y(K)/D(K)-Z(K)*P(K)
7 C(4,K)=Y(K+1)/D(K)-Z(K+1)*P(K)
RETURN
END

```

FORTRAN IV G LEVEL 21

SPLINE

SUBROUTINE SPLINE(X,Y,M,C,XINT,YINT)

REAL\*8 X,Y,XINT

DIMENSION X(5),Y(5),C(4,5)

IF(XINT-X(1))7,1,2

1 YINT=Y(1)

RETURN

2 K=1

3 IF(XINT-X(K+1))6,4,5

4 YINT=Y(K+1)

RETURN

5 K=K+1

IF(M-K)7,73

6 YINT=(X(K+1)-XINT)\*(C(1,K)\*(X(K+1)-XINT)\*\*2+C(3,K))

YINT=YINT+(XINT-X(K))\*(C(2,K)\*(XINT-X(K))\*\*2+C(4,K))

RETURN

7 WRITE(6,101)

STOP

101 FORMAT(1X,'OUT OF RANGE FOR INTERPOLATION')

END

### 2.3. Experimental and Results

Coal samples supplied by the National Coal Board\*\* have been run on the Du Pont Model 21-110B double-focusing high-resolution mass spectrometer of Mattauch-Herzog geometry. This instrument permits simultaneous photoplate recording of all ions on Ionomer plates placed in the focal plane with increased sensitivity at high mass-to-charge ratio. The samples were introduced by the Lumpkin cup system. The instrument was run at an electron voltage of 70 eV<sub>(1)</sub>, temperature of ion source around 300°C, accelerating voltage of 8 KV, with a resolving power of 12,000 for plate runs.

The masses of the ions were first calculated by a variation of the Biemann method<sup>20</sup>. Photoplate recordings of high-resolution spectra were measured automatically using a Grant-Datex comparator-microdensitometer. Data were recorded on magnetic tapes for processing by an IBM 1108 computer at Carnegie Melton University, U.S.A. Perfluorokerosene was used for calibration of the mass-to-charge ratio scale. The high-resolution data were then computed using a variation of the Shell Development Laboratory programme, which is based on a variation of the Biemann method devised by Tunnicliff and Wadsworth<sup>31</sup>. This operation was carried out at the Pittsburgh Energy Research Centre in the United States of America.\*\*\*

-----

\*\* Coal Research Establishment,

Stoke Orchard, Cheltenham, Gloucestershire, U.K.

(1)  $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$  (S.I. Units).

\*\*\*

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Pennsylvania 15213,  
U.S.A.

Gratitude is recorded for the assistance given in this work by Mr. A.G. Sharkey, Jr., Mr. Albert MacLean and Miss Janet Schulz.

Using the same readings of distances measured by the comparator, the masses of the ions were calculated by the mathematical method already described. An IBM 370/158 computer at Edinburgh University with a data link for Glasgow University was used for the computation of data.

The results of both methods were then compared.

In tables 2.1-2.5, the final data output obtained by the spline-fit interpolation method and the variation of the Biemann method for the calculation of masses of several ions for five coal extraction fractions is shown. Each table comprises four columns. The first lists the line positions or distances used in the calculations. The second lists the monotonically increasing masses  $M_1$  of the ions in the 80 to 400 region calculated by the spline-fit interpolation method. The third lists the corresponding values  $M_2$  of the masses of the same ions calculated by the variation of the Biemann method. In the fourth column of these tables the difference between  $M_2$  and  $M_1$  is listed for comparison. The mean differences and the standard deviations were also evaluated for all the measurements made. These simple calculations of mean differences and standard deviations were evaluated by a computer programme shown on page 104. The mean differences and the standard deviations are displayed for all coal extraction fractions samples, in millimass units, in table 2.6.

TABLE 2.1. - FINAL DATA OUTPUT FOR SPECTRUM E

<u>reference distances</u>	<u>reference masses</u>		
17.16717	84.96565		
91.71401	169.99216		
146.34439	250.99183		
210.68485	366.97920		
229.41536	404.97599		
5			
0.1165E-04	0.1619E-04	0.1393E-04	0.4857E-04
0.1186E-04	0.1640E-04	0.1414E-04	0.4878E-04
0.1075E 01	0.3063E 01	0.3843E 01	0.1958E 02
0.2214E 01	0.4545E 01	0.5645E 01	0.2160E 02

distance	mass $M_1$	mass $M_2$	$M_2 - M_1$
17.23412	85.02892	85.03120	0.00228
17.27254	85.06523	85.06748	0.00225
17.31098	85.10161	85.10380	0.00219
18.27508	86.01605	86.01724	0.00119
18.29838	86.03819	86.03938	0.00119
16.33582	86.07382	86.07495	0.00113
18.36899	86.10536	86.10648	0.00112
19.33096	87.02309	87.02328	0.00019
19.33661	87.02849	87.02868	0.00019
20.38318	88.03242	88.03171	-0.00071
20.90404	88.53419	88.53307	-0.00112
21.42722	89.03961	89.03810	-0.00151
22.46475	90.04616	90.04395	-0.00221
22.97849	90.54663	90.54411	-0.00252
23.50068	91.05676	91.05393	-0.00283
24.52725	92.06375	92.06040	-0.00335
25.47458	92.99788	92.99520	-0.00268
25.55028	93.07274	93.06896	-0.00378
26.01246	93.53035	93.52642	-0.00393
26.51912	94.03331	94.02921	-0.00410
26.53034	94.04446	94.04035	-0.00411
26.56701	94.08092	94.07681	-0.00411
27.02586	94.53767	94.53344	-0.00423
27.50319	95.01399	95.00965	-0.00434
27.52932	95.04012	95.03575	-0.00437
27.54122	95.05200	95.04764	-0.00436
27.57807	95.08884	95.08446	-0.00438
28.02870	95.53978	95.53532	-0.00446
28.58278	96.09570	96.09117	-0.00453
29.03145	96.54704	96.54245	-0.00459
29.58396	97.10428	97.09966	-0.00462
30.48627	98.01775	98.01312	-0.00463
30.54307	98.07539	98.07296	-0.00243
30.57759	98.11044	98.10798	-0.00246
31.47721	99.02585	99.02300	-0.00285
31.56913	99.11961	99.11673	-0.00288
32.42619	99.99606	99.99286	-0.00320
32.46288	100.03366	100.03046	-0.00320
32.51867	100.09087	100.08763	-0.00324
32.95225	100.53593	100.53256	-0.00337
33.40674	101.00349	101.00143	-0.00206
33.44225	101.04007	101.03658	-0.00349
33.92720	101.54028	101.53666	-0.00362
34.41542	102.04509	102.04137	-0.00372
34.89331	102.54562	102.54182	-0.00380
35.37766	103.04369	103.03982	-0.00387
35.38950	103.05602	103.05213	-0.00389
36.32001	104.02634	104.02238	-0.00396
36.32649	104.03311	104.02915	-0.00396
36.35569	104.06363	104.05967	-0.00396
37.28274	105.03503	105.03106	-0.00397
37.31754	105.07159	105.06761	-0.00398
37.75162	105.52808	105.52409	-0.00399
38.22818	106.03035	106.02640	-0.00395
38.27377	106.07846	106.07452	-0.00394
38.70639	106.53555	106.53167	-0.00388
39.18084	107.03798	107.03414	-0.00384
39.19276	107.05063	107.04679	-0.00384



39.22653	107.08644	107.08260	-0.00384
39.65333	107.53952	107.53574	-0.00378
40.12803	108.04456	108.04087	-0.00369
40.14098	108.05835	108.05680	-0.00155
40.17456	108.09413	108.09257	-0.00156
40.59709	108.54477	108.54313	-0.00164
41.05729	109.03664	109.03493	-0.00171
41.06836	109.04848	109.04678	-0.00170
41.08418	109.06541	109.06370	-0.00171
41.11862	109.10228	109.10056	-0.00172
41.53770	109.55130	109.54954	-0.00176
41.98867	110.03552	110.03371	-0.00181
42.05663	110.10858	110.10677	-0.00181
42.90496	111.02266	111.02080	-0.00186
42.99223	111.11691	111.11504	-0.00187
43.80110	111.99234	111.99360	0.00126
43.83600	112.03020	112.02833	-0.00187
43.92110	112.12253	112.12065	-0.00188
44.29946	112.53343	112.53158	-0.00185
44.72844	113.00023	112.99840	-0.00183
44.76241	113.03723	113.03541	-0.00182
44.84893	113.13152	113.12970	-0.00182
45.22144	113.53789	113.53611	-0.00178
45.68185	114.04114	114.03943	-0.00171
46.60193	115.05019	115.04862	-0.00157
47.05666	115.55054	115.54906	-0.00148
47.51273	116.05344	116.05207	-0.00137
47.95249	116.53938	116.54160	0.00222
48.36210	116.99294	116.99504	0.00210
48.41811	117.05504	117.05712	0.00208
48.43025	117.06850	117.07057	0.00207
48.84126	117.52461	117.52661	0.00200
49.29449	118.02864	118.03052	0.00188
49.30471	118.04002	118.04190	0.00188
49.32578	118.06348	118.06535	0.00187
49.33675	118.07570	118.07756	0.00186
49.74672	118.53261	118.53441	0.00180
50.15637	118.99007	118.99179	0.00172
50.19437	119.03223	119.03395	0.00172
50.24043	119.08405	119.08576	0.00171
50.64595	119.53795	119.53959	0.00164
51.05137	119.99258	119.99417	0.00159
51.09435	120.04082	120.04242	0.00160
51.10737	120.05545	120.05703	0.00158
51.13742	120.08917	120.09077	0.00160
51.54050	120.54224	120.54378	0.00154
51.97031	121.02628	121.02778	0.00150
51.98648	121.04449	121.04601	0.00152
52.00267	121.06276	121.06426	0.00150
52.03493	121.09914	121.10063	0.00149
52.43332	121.54880	121.55027	0.00147
52.86232	122.03392	122.03538	0.00146
52.88101	122.05508	122.05654	0.00146
52.89487	122.07079	122.07223	0.00144
52.92595	122.10597	122.10742	0.00145
53.32343	122.55646	122.55789	0.00143
53.75030	123.04118	123.04262	0.00144
53.77004	123.06361	123.06506	0.00145

53.81436	123.11401	123.11545	0.00144
54.19450	123.54660	123.54805	0.00145
54.58341	123.98996	123.99360	0.00364
54.61627	124.02745	124.02893	0.00148
54.63413	124.04784	124.04931	0.00147
54.69789	124.12062	124.12209	0.00147
55.49768	125.03537	125.03689	0.00152
55.57946	125.12909	125.13062	0.00153
55.93331	125.53503	125.53660	0.00157
56.37376	126.04077	126.04239	0.00162
56.45628	126.13618	126.13782	0.00164
56.80789	126.54117	126.54285	0.00168
57.24643	127.04718	127.04894	0.00176
57.33069	127.14453	127.14884	0.00431
57.67930	127.54767	127.55188	0.00421
58.11551	128.05299	128.05711	0.00412
58.53325	128.53787	128.54188	0.00401
58.54817	128.55521	128.55922	0.00401
58.97995	129.05737	129.06129	0.00392
59.00875	129.09091	129.09481	0.00390
59.39876	129.54539	129.54923	0.00384
59.83862	130.05894	130.06269	0.00375
59.85139	130.07385	130.07761	0.00376
60.24171	130.53046	130.53413	0.00367
60.63188	130.98767	130.99128	0.00361
60.67929	131.04327	131.04688	0.00361
60.71095	131.08041	131.08403	0.00362
61.10038	131.53772	131.54128	0.00356
61.48521	131.99042	131.99536	0.00494
61.52612	132.03857	132.04209	0.00352
61.53749	132.05196	132.05548	0.00352
61.56801	132.08791	132.09141	0.00350
61.95182	132.54034	132.54381	0.00347
62.34335	133.00267	133.00610	0.00343
62.37864	133.04437	133.04781	0.00344
62.39268	133.06099	133.06440	0.00341
62.42249	133.09622	133.09964	0.00342
62.80348	133.54704	133.55044	0.00340
63.22843	134.05078	134.05414	0.00336
63.27372	134.10452	134.10788	0.00336
63.65205	134.55389	134.55724	0.00335
64.05973	135.03896	135.04229	0.00333
64.07408	135.05605	135.05939	0.00334
64.09016	135.07520	135.07853	0.00333
64.49836	135.56183	135.56516	0.00333
64.90325	136.04539	136.04871	0.00332
64.92261	136.06854	136.07186	0.00332
64.96499	136.11920	136.12252	0.00332
65.72811	137.03319	137.03652	0.00333
65.80650	137.12724	137.13058	0.00334
66.56587	138.04010	138.04347	0.00337
66.98057	138.53990	138.54436	0.00448
67.40006	139.04640	139.05077	0.00437
67.48018	139.14323	139.14759	0.00436
67.81351	139.54651	139.55077	0.00426
68.22904	140.05003	140.05419	0.00416
68.31210	140.15080	140.15494	0.00414
68.64452	140.55443	140.55849	0.00406

69.06118	141.06117	141.06511	0.00394
69.14142	141.15884	141.16280	0.00396
69.47190	141.56157	141.56543	0.00386
69.88843	142.06996	142.07374	0.00378
70.63757	142.98662	142.99200	0.00538
70.70958	143.07489	143.07851	0.00362
71.08614	143.53693	143.54047	0.00354
71.45793	143.99384	143.99731	0.00347
71.50511	144.05186	144.05535	0.00349
71.90264	144.54132	144.54473	0.00341
72.27634	145.00218	145.00555	0.00337
72.31115	145.04515	145.04850	0.00335
72.32210	145.05867	145.06203	0.00336
72.35282	145.09659	145.09994	0.00335
72.71775	145.54750	145.55081	0.00331
73.12603	146.05283	146.05606	0.00323
73.13900	146.06889	146.07213	0.00324
73.53118	146.55513	146.55832	0.00319
73.85517	146.95744	146.96059	0.00315
73.93749	147.05974	147.06319	0.00345
73.95092	147.07643	147.07989	0.00346
73.97996	147.11253	147.11600	0.00347
74.34185	147.56281	147.56642	0.00361
74.74819	148.06920	148.07298	0.00378
75.51014	149.02112	149.02523	0.00411
75.55617	149.07870	149.08285	0.00415
75.59585	149.12839	149.13254	0.00415
76.27985	149.98584	149.99030	0.00446
76.30985	150.02351	150.02798	0.00447
76.32640	150.04430	150.04877	0.00447
76.39905	150.13553	150.14004	0.00451
77.08163	150.99409	150.99823	0.00414
77.12501	151.04875	151.05360	0.00485
77.20107	151.14459	151.14948	0.00489
77.92192	152.05443	152.05967	0.00524
77.92937	152.06384	152.06909	0.00525
77.99860	152.15137	152.15666	0.00529
78.31843	152.55606	152.56152	0.00546
78.71737	153.06161	153.06727	0.00566
78.79509	153.16020	153.16590	0.00570
79.11279	153.56354	153.56940	0.00586
79.50756	154.06544	154.07153	0.00609
79.58819	154.16806	154.17418	0.00612
80.23231	154.98906	154.99552	0.00646
80.30385	155.08038	155.08689	0.00651
81.08425	156.07831	156.08525	0.00694
81.09391	156.09068	156.09764	0.00696
81.85064	157.06146	157.06885	0.00739
81.87840	157.09712	157.10346	0.00634
82.62466	158.05756	158.06379	0.00623
82.63444	158.07016	158.07639	0.00623
83.40527	159.06534	159.07148	0.00614
83.41555	159.07863	159.08477	0.00614
83.42444	159.09013	159.09627	0.00614
84.18306	160.07269	160.07874	0.00605
84.18933	160.08083	160.08688	0.00605
84.99732	161.13072	161.13668	0.00696
85.65551	161.98851	161.99040	0.00189

85.73281	162.08940	162.09531	0.00591
86.42659	162.99635	163.00218	0.00583
86.46998	163.05316	163.05898	0.00582
86.50371	163.09732	163.10315	0.00583
86.54150	163.14682	163.15264	0.00582
87.23537	164.05685	164.06262	0.00577
87.30943	164.15414	164.15990	0.00576
88.00534	165.06969	165.07541	0.00572
88.07627	165.16315	165.16885	0.00570
88.76629	166.07375	166.07941	0.00566
88.83910	166.16998	166.17819	0.00821
89.49173	167.03380	167.04169	0.00789
89.52534	167.07835	167.08622	0.00787
89.60122	167.17896	167.18678	0.00782
90.26284	168.05736	168.06487	0.00751
90.28037	168.08067	168.08816	0.00749
90.29008	168.09358	168.10107	0.00749
90.36054	168.18727	168.19473	0.00746
90.96307	168.98958	168.99673	0.00715
91.04642	169.10071	169.70783	0.60712
91.11742	169.19540	169.20249	0.00709
91.69947	169.97273	169.97954	0.00681
91.79270	170.09740	170.10416	0.00676
92.94615	171.64372	171.64992	0.00620
92.97016	171.67598	171.68218	0.00620
93.19027	171.97191	171.97798	0.00607
93.26831	172.07687	172.08292	0.00605
94.01663	173.08513	173.09080	0.00567
94.68747	173.99152	173.99688	0.00536
94.72939	174.04823	174.05357	0.00534
94.76173	174.09200	174.09732	0.00532
95.43118	174.99916	175.00414	0.00498
95.47530	175.05902	175.06400	0.00498
96.21461	176.06380	176.06840	0.00460
96.24735	176.10835	176.11295	0.00460
96.94910	177.06488	177.06912	0.00424
97.02261	177.16522	177.16943	0.00421
97.68876	178.07590	178.08448	0.00858
97.75952	178.17278	178.18130	0.00852
98.42404	179.08383	179.09187	0.00804
98.49506	179.18134	179.18932	0.00798
99.13332	180.05882	180.06635	0.00753
99.15161	180.08401	180.09151	0.00750
99.80955	180.99089	180.98880	0.00209
99.86352	181.06538	181.07236	0.00698
99.89115	181.08972	181.09668	0.00696
99.95832	181.19626	181.20317	0.00691
100.53506	181.99358	182.00004	0.00646
100.58798	182.06683	182.07325	0.00642
100.61085	182.09848	182.10489	0.00641
101.26526	183.00558	183.01148	0.00590
101.31164	183.06996	183.07582	0.00586
101.41437	183.21257	183.21837	0.00580
101.80131	183.75031	183.75580	0.00549
102.03637	184.07735	184.08266	0.00531
102.75865	185.08412	185.08888	0.00476
102.77555	185.10771	185.11246	0.00475
103.40790	185.99146	185.99573	0.00427

103.48005	186.09244	186.09053	-0.00191
104.16761	187.05602	187.05423	-0.00179
104.19919	187.10036	187.09855	-0.00181
104.88368	188.06224	188.06055	-0.00169
104.91572	188.10735	188.10564	-0.00171
105.60072	189.07267	189.07099	-0.00158
105.66595	189.16463	189.16303	-0.00160
106.30732	190.07086	190.06937	-0.00149
107.01923	191.07933	191.07795	-0.00138
107.09113	191.18134	191.17995	-0.00139
107.72565	192.08270	192.08140	-0.00130
107.73516	192.09624	192.09492	-0.00132
107.79957	192.18785	192.18655	-0.00130
108.36335	192.99075	192.98880	-0.00195
108.43287	193.08987	193.08866	-0.00121
108.44204	193.10295	193.10173	-0.00122
108.50789	193.19687	193.19566	-0.00121
109.13931	194.09859	194.09745	-0.00114
109.82174	195.07555	195.07449	-0.00106
109.84025	195.10208	195.10102	-0.00106
110.52024	196.07808	196.07710	-0.00098
110.53521	196.09959	196.09861	-0.00098
110.54495	196.11360	196.11262	-0.00098
111.22006	197.08511	197.08420	-0.00091
111.23502	197.10667	197.10546	-0.00121
111.91837	198.09258	198.09146	-0.00112
112.61472	199.09979	199.09880	-0.00099
113.28043	200.06514	200.06420	-0.00094
113.30929	200.10704	200.10611	-0.00093
113.92048	200.99548	200.99503	-0.00045
113.97102	201.06905	201.06819	-0.00086
114.00247	201.11481	201.11398	-0.00083
114.66232	202.07652	202.07576	-0.00076
115.34877	203.07945	203.07876	-0.00069
116.03338	204.08220	204.08159	-0.00061
116.65113	204.98917	204.98861	-0.00056
116.71675	205.08563	205.08507	-0.00056
116.79065	205.19429	205.19374	-0.00055
117.40126	206.09323	206.09274	-0.00049
118.08379	207.10040	207.09996	-0.00044
118.15844	207.21071	207.21028	-0.00043
118.74284	208.07529	208.07489	-0.00040
118.76651	208.11035	208.10995	-0.00040
119.44414	209.11523	209.11507	-0.00016
120.10021	210.09047	210.09037	-0.00010
120.11816	210.11719	210.11709	-0.00010
120.74841	211.05627	211.05624	-0.00003
120.76101	211.07507	211.07503	-0.00004
120.77646	211.09811	211.09808	-0.00003
121.37210	211.98767	211.98720	-0.00047
121.43539	212.08231	212.08232	0.00001
121.45174	212.10675	212.10677	0.00002
122.04477	212.99455	212.99459	0.00004
122.09607	213.07144	213.07148	0.00004
122.12453	213.11411	213.11415	0.00004
122.75705	214.06335	214.06344	0.00009
122.76831	214.08028	214.08035	0.00007
123.43516	215.08342	215.08351	0.00009

124.09927	216.08479	216.08489	0.00010
124.69774	216.98920	216.98869	-0.00051
124.76440	217.09006	217.08957	-0.00049
124.83403	217.19543	217.19495	-0.00048
125.41734	218.07922	218.07881	-0.00041
125.43006	218.09850	218.09810	-0.00040
126.01527	218.98703	218.98672	-0.00031
126.07044	219.07088	219.07058	-0.00030
126.09101	219.10216	219.10186	-0.00030
126.16280	219.21132	219.21102	-0.00030
126.73085	220.07599	220.07577	-0.00022
126.75314	220.10994	220.10972	-0.00022
127.39108	221.08315	221.08298	-0.00017
127.41468	221.11919	221.11904	-0.00015
127.48514	221.22681	221.22666	-0.00015
128.05194	222.09358	222.09349	-0.00009
128.07211	222.12447	222.12437	-0.00010
128.70846	223.09972	223.09968	-0.00004
128.73253	223.13666	223.13663	-0.00003
129.28691	223.98813	223.98720	-0.00093
129.33592	224.06348	224.06347	-0.00001
129.36205	224.10365	224.10365	0.0
129.38286	224.13567	224.13566	-0.00001
129.94120	224.99516	224.99518	0.00002
129.99374	225.07613	225.07615	0.00002
130.01857	225.11440	225.11442	0.00002
130.64361	226.07880	226.07887	0.00007
130.66942	226.11867	226.11872	0.00005
131.29092	227.07979	227.07986	0.00007
131.32427	227.13142	227.13148	0.00006
131.94050	228.08653	228.08660	0.00007
132.58869	229.09338	229.09298	-0.00040
133.23382	230.09772	230.09743	-0.00029
133.80302	230.98569	230.98560	-0.00009
133.87610	231.09982	231.09964	-0.00018
134.44465	231.98875	231.98865	-0.00010
134.50160	232.07788	232.07779	-0.00009
134.52139	232.10886	232.10877	-0.00009
135.09075	233.00101	233.00101	0.0
135.14445	233.08525	233.08524	-0.00001
135.16510	233.11765	233.11763	-0.00002
135.23446	233.22649	233.22647	-0.00002
135.78124	234.08531	234.08537	0.00006
135.80628	234.12468	234.12474	0.00006
136.42507	235.09863	235.09874	0.00011
136.44689	235.13300	235.13313	0.00013
136.51576	235.24155	235.24167	0.00012
136.98834	235.98698	235.98715	0.00017
137.06379	236.10609	236.10628	0.00019
137.08201	236.13487	236.13505	0.00018
137.70121	237.11371	237.11392	0.00021
137.72440	237.15042	237.15063	0.00021
138.30125	238.06422	238.06445	0.00023
138.33472	238.11729	238.11729	0.0
138.94523	239.08649	239.08659	0.00010
138.97243	239.12971	239.12982	0.00011
139.57267	240.08464	240.08486	0.00022
139.59941	240.12723	240.12745	0.00022

140.20233	241.08844	241.08876	0.00032
140.21540	241.10930	241.10962	0.00032
140.83260	242.09535	242.09575	0.00040
141.38933	242.98656	242.98560	-0.00096
141.44150	243.07016	243.07061	0.00045
141.46331	243.10510	243.10557	0.00047
142.01493	243.98999	243.99049	0.00050
142.07533	244.08698	244.08750	0.00052
142.09108	244.11227	244.11278	0.00051
142.70034	245.09175	245.09231	0.00056
142.71947	245.12254	245.12310	0.00056
143.32157	246.09254	246.09313	0.00059
143.34083	246.12361	246.12420	0.00059
143.92975	247.07431	247.07491	0.00060
143.94637	247.10117	247.10069	-0.00048
143.96741	247.13518	247.13470	-0.00048
144.03368	247.24228	247.24183	-0.00045
144.55636	248.08792	248.08759	-0.00033
144.56961	248.10938	248.10905	-0.00033
144.58500	248.13429	248.13397	-0.00032
145.16793	249.07922	249.07904	-0.00018
145.18976	249.11464	249.11446	-0.00018
145.21136	249.14969	249.14953	-0.00016
145.78365	250.07928	250.07923	-0.00005
145.82687	250.14957	250.14951	-0.00006
146.39494	251.07417	251.07423	0.00006
146.42968	251.13078	251.13083	0.00005
147.01824	252.09067	252.09083	0.00016
147.04435	252.13330	252.13346	0.00016
147.63214	253.09389	253.09412	0.00023
148.24623	254.09943	254.09974	0.00031
148.78641	254.98564	254.98600	0.00036
148.85760	255.10255	255.10291	0.00036
149.44900	256.07471	256.07521	0.00050
149.47200	256.11255	256.11306	0.00051
150.05993	257.08105	257.08159	0.00054
150.08443	257.12134	257.12199	0.00065
150.67196	258.09131	258.09177	0.00046
150.69175	258.12378	258.12446	0.00068
151.28245	259.10083	259.10139	0.00056
151.30335	259.13550	259.13585	0.00035
151.87507	260.08276	260.08326	0.00050
151.89046	260.10840	260.10878	0.00038
152.49846	261.11792	261.11829	0.00037
152.51949	261.15283	261.15323	0.00040
153.09109	262.10376	262.10416	0.00040
153.10090	262.12012	262.12049	0.00037
153.62407	262.99194	262.99183	-0.00011
153.68360	263.09131	263.09171	0.00040
153.70778	263.13159	263.13204	0.00045
153.72857	263.16626	263.16674	0.00048
154.27837	264.08447	264.08492	0.00045
154.30700	264.13232	264.13276	0.00044
154.88273	265.09570	265.09607	0.00037
154.91304	265.14648	265.14683	0.00035
155.48298	266.10205	266.10227	0.00022
155.51053	266.14844	266.14772	-0.00072
156.00952	266.98633	266.98583	-0.00050

156.08184	267.10791	267.10741	-0.00050
156.67897	268.11279	268.11234	-0.00045
157.19351	268.98047	268.97980	-0.00067
157.20213	268.99487	268.99433	-0.00054
157.25554	269.08496	269.08447	-0.00049
157.27651	269.12036	269.11986	-0.00050
157.83676	270.06689	270.06623	-0.00066
157.84949	270.08838	270.08777	-0.00061
157.87259	270.12744	270.12682	-0.00062
158.43221	271.07446	271.07392	-0.00054
158.44724	271.10010	271.09937	-0.00073
159.04117	272.10718	272.10641	-0.00077
159.06004	272.13916	272.13845	-0.00071
159.61744	273.08618	273.08533	-0.00085
159.63511	273.11621	273.11538	-0.00083
159.65577	273.15112	273.15050	-0.00062
160.14559	273.98486	273.98400	-0.00086
160.21563	274.10425	274.10334	-0.00091
160.22797	274.12524	274.12435	-0.00089
160.24233	274.14966	274.14882	-0.00084
160.73597	274.99146	274.99041	-0.00105
160.78364	275.07275	275.07176	-0.00099
160.79771	275.09668	275.09579	-0.00089
160.81807	275.13135	275.13052	-0.00083
160.83892	275.16699	275.16610	-0.00089
161.38245	276.09570	276.09457	-0.00113
161.40496	276.13403	276.13306	-0.00097
161.42325	276.16528	276.16433	-0.00095
161.96291	277.08911	277.08786	-0.00125
161.97501	277.11108	277.10996	-0.00112
161.99684	277.14722	277.14597	-0.00125
162.55238	278.09985	278.09842	-0.00143
162.58237	278.15112	278.14989	-0.00123
163.13892	279.10718	279.10579	-0.00139
163.16997	279.16064	279.15917	-0.00147
163.72445	280.11499	280.11326	-0.00173
164.22923	280.98511	280.98239	-0.00272
164.30854	281.12207	281.12009	-0.00198
164.80970	281.98755	281.98543	-0.00212
164.88495	282.11768	282.11547	-0.00221
164.89598	282.13672	282.13454	-0.00218
165.45392	283.10205	283.09974	-0.00231
165.47400	283.13672	283.13451	-0.00221
166.02093	284.08496	284.08234	-0.00262
166.03366	284.10693	284.10442	-0.00251
166.05399	284.14233	284.13968	-0.00265
166.59989	285.09033	285.08743	-0.00290
166.61577	285.11792	285.11501	-0.00291
166.63649	285.15381	285.15102	-0.00279
167.11545	285.98706	285.98395	-0.00311
167.17975	286.09888	286.09586	-0.00302
167.19548	286.12646	286.12324	-0.00322
167.21268	286.15625	286.15318	-0.00307
167.74434	287.08301	287.07946	-0.00355
167.77468	287.13574	287.13238	-0.00336
167.79459	287.17065	287.16711	-0.00354
168.31810	288.08447	288.08081	-0.00366
168.34087	288.12427	288.12057	-0.00370



168.35182	288.14355	288.13971	-0.00384
169.47450	290.10889	290.05604	-0.05285
169.50118	290.15552	290.10290	-0.05262
170.04784	291.11499	291.06357	-0.05142
170.07847	291.16895	291.11744	-0.05151
170.62022	292.12134	292.07117	-0.05017
171.11386	292.99072	292.94156	-0.04916
171.19193	293.12842	293.07932	-0.04910
171.72895	294.07593	294.02791	-0.04802
171.76251	294.13501	294.08724	-0.04777
172.31425	295.11035	295.06355	-0.04680
172.33468	295.14648	295.09973	-0.04675
172.88075	296.11328	296.06767	-0.04561
172.90184	296.15063	296.10509	-0.04554
173.45201	297.12646	297.08197	-0.04449
173.47211	297.16211	297.11769	-0.04442
174.00561	298.10986	298.06658	-0.04328
174.01779	298.13159	298.08826	-0.04333
174.03650	298.16479	298.12157	-0.04322
174.56957	299.11353	299.07132	-0.04221
174.58576	299.14233	299.10020	-0.04213
174.60609	299.17871	299.13645	-0.04226
175.12608	300.10571	300.06445	-0.04126
175.15096	300.14990	300.10890	-0.04100
175.16763	300.17969	300.13868	-0.04101
175.68485	301.10327	301.06330	-0.03997
175.69592	301.12305	301.08311	-0.03994
175.71595	301.15894	301.11894	-0.04000
175.73568	301.19434	301.15425	-0.04009
176.25033	302.11475	302.07585	-0.03890
176.27311	302.15552	302.11666	-0.03886
176.81377	303.12451	303.08645	-0.03806
177.37358	304.12915	304.09222	-0.03693
177.85593	304.99634	304.96017	-0.03617
177.93244	305.13379	305.09797	-0.03582
178.49240	306.14233	306.10737	-0.03496
179.03081	307.11353	307.07953	-0.03400
179.05054	307.14917	307.11517	-0.03400
179.57519	308.09692	308.06403	-0.03289
179.60597	308.15259	308.11976	-0.03283
180.14450	309.12744	309.09534	-0.03210
180.16484	309.16431	309.13222	-0.03209
180.70001	310.13452	310.10331	-0.03121
180.71893	310.16870	310.13767	-0.03103
181.25755	311.14673	311.11665	-0.03008
181.27735	311.18286	311.15266	-0.03020
181.80977	312.15112	312.12195	-0.02917
181.82855	312.18530	312.15616	-0.02914
182.28001	313.00781	312.97930	-0.02851
182.38638	313.20166	313.17340	-0.02826
182.88820	314.11743	314.08995	-0.02748
182.90767	314.15308	314.12552	-0.02756
182.91953	314.17480	314.14720	-0.02760
182.93495	314.20288	314.17538	-0.02750
183.44075	315.12744	315.10069	-0.02675
183.45295	315.14966	315.12302	-0.02664
183.47197	315.18457	315.15783	-0.02674
183.99429	316.14087	316.11488	-0.02599

184.46602	317.00562	316.98049	-0.02513
184.53707	317.13599	317.11097	-0.02502
185.09008	318.15161	318.12746	-0.02415
185.55209	319.00146	318.97794	-0.02352
185.63656	319.15698	319.13356	-0.02342
186.18307	320.16406	320.14130	-0.02276
186.72927	321.17212	321.15010	-0.02202
187.27113	322.17358	322.15245	-0.02113
187.79840	323.14990	323.12935	-0.02055
187.81750	323.18530	323.16476	-0.02054
188.35767	324.18701	324.16713	-0.01988
188.88390	325.16431	325.14516	-0.01915
188.90284	325.19946	325.18038	-0.01908
189.44170	326.20190	326.18349	-0.01841
189.96618	327.17920	327.16131	-0.01789
192.00703	330.99585	330.98029	-0.01556
193.16175	333.16553	333.15099	-0.01454
194.23112	335.18115	335.16764	-0.01351
194.76171	336.18335	336.17051	-0.01284
195.29636	337.19507	337.18260	-0.01247
198.34380	342.99097	342.98079	-0.01018
204.56790	354.98535	354.98095	-0.00440
211.69214	368.97363	368.97463	0.00100
217.69335	380.97192	380.97600	0.00408
223.59909	392.97144	392.97599	0.00455

TABLE 2.2 - FINAL DATA OUTPUT FOR SPECTRUM F

<u>reference distances</u>	<u>reference masses</u>		
17.14896	84.96565		
91.68561	169.99219		
146.31281	250.99183		
198.31113	342.97919		
229.38543	404.97599		
5			
0.1167E-04	0.1618E-04	0.1720E-04	0.2926E-04
0.1186E-04	0.1637E-04	0.1748E-04	0.2954E-04
0.1075E 01	0.3064E 01	0.4780E 01	0.1101E 02
0.2215E 01	0.4546E 01	0.6549E 01	0.1300E 02

17.14896	84.96565	0.1167E-04	0.2926E-04
91.68561	169.99219	0.1186E-04	0.2954E-04
146.31281	250.99183	0.1075E 01	0.1101E 02
198.31113	342.97919	0.2215E 01	0.1300E 02
229.38543	404.97599		
0.1167E-04	0.1618E-04	0.1720E-04	0.2926E-04
0.1186E-04	0.1637E-04	0.1748E-04	0.2954E-04
0.1075E 01	0.3064E 01	0.4780E 01	0.1101E 02
0.2215E 01	0.4546E 01	0.6549E 01	0.1300E 02

<u>distance</u>	<u>mass <math>M_1</math></u>	<u>mass <math>M_2</math></u>	<u><math>M_2 - M_1</math></u>
17.21609	85.02905	85.03143	0.00238
17.25413	85.06503	85.06736	0.00233
17.29243	85.10126	85.10355	0.00229
18.25669	86.01579	86.01729	0.00150
18.27889	86.03691	86.03839	0.00148
18.31716	86.07330	86.07476	0.00146
18.35077	86.10530	86.10671	0.00141
19.31370	87.02390	87.02459	0.00069
19.33573	87.04497	87.04565	0.00068
19.83913	87.52718	87.52751	0.00033
20.36449	88.03183	88.03183	0.0
20.88541	88.53366	88.53332	-0.00034
21.40788	89.03839	89.03776	-0.00063
21.92494	89.53931	89.53840	-0.00091
22.44594	90.04546	90.04428	-0.00118
22.95877	90.54504	90.54364	-0.00140
23.48046	91.05467	91.05306	-0.00161
24.47186	92.02708	92.02511	-0.00197
24.50710	92.06174	92.05977	-0.00197
25.45489	92.99635	92.99412	-0.00223
25.49344	93.03445	93.03222	-0.00223
25.52962	93.07024	93.06798	-0.00226
25.99271	93.52878	93.52642	-0.00236
26.49923	94.03160	94.02915	-0.00245
26.51129	94.04358	94.04115	-0.00243
26.54644	94.07854	94.07609	-0.00245
27.00571	94.53572	94.53321	-0.00251
27.48281	95.01184	95.00928	-0.00256
27.50964	95.03865	95.03608	-0.00257
27.52155	95.05055	95.04799	-0.00256
27.55757	95.08655	95.08399	-0.00256
28.00871	95.53804	95.53543	-0.00261
28.51413	96.04509	96.04248	-0.00261
28.52702	96.05864	96.05603	-0.00261
28.56208	96.09328	96.09065	-0.00263
29.01099	96.54486	96.54226	-0.00260
29.49815	97.03615	97.03356	-0.00259
29.52727	97.06555	97.06296	-0.00259
29.56280	97.10143	97.09885	-0.00258
30.46589	98.01575	98.01325	-0.00250
30.52199	98.07268	98.07258	-0.00010
30.55668	98.10788	98.10778	-0.00010
31.45668	99.02374	99.02333	-0.00041
31.51252	99.08072	99.08027	-0.00045
31.54814	99.11705	99.11660	-0.00045
31.94957	99.52711	99.52655	-0.00056
32.40528	99.99365	99.99296	-0.00069
32.44229	100.03159	100.03088	-0.00071
32.46285	100.05266	100.05196	-0.00070
32.49767	100.08836	100.08766	-0.00070
32.52871	100.12019	100.11948	-0.00071
32.93111	100.53329	100.53251	-0.00078
33.38542	101.00075	101.00084	-0.00091
33.42136	101.03775	101.03685	-0.00090
33.44325	101.06032	101.05941	-0.00091
33.90702	101.53873	101.53775	-0.00098
34.39404	102.04236	102.04130	-0.00106
34.87708	102.54308	102.54198	-0.00110

35.35612	103.04086	103.03973	-0.00113
35.36901	103.05428	103.05315	-0.00113
36.29981	104.02501	104.02384	-0.00117
36.32104	104.04720	104.04604	-0.00116
36.33435	104.06111	104.05996	-0.00115
37.26067	105.03186	105.03073	-0.00113
37.29605	105.06902	105.06789	-0.00113
37.73008	105.52548	105.52440	-0.00108
38.20780	106.02905	106.02800	-0.00105
38.21748	106.03926	106.03822	-0.00104
38.24217	106.06532	106.06429	-0.00103
38.25181	106.07549	106.07445	-0.00104
38.25736	106.08136	106.08032	-0.00104
38.68472	106.53296	106.53198	-0.00098
39.15912	107.03539	107.03448	-0.00091
39.17193	107.04895	107.04807	-0.00088
39.20458	107.08357	107.08270	-0.00087
39.63170	107.53706	107.53626	-0.00080
40.10640	108.04216	108.04147	-0.00069
40.11911	108.05571	108.05719	0.00148
40.15204	108.09079	108.09227	0.00148
40.57498	108.54192	108.54334	0.00142
41.03528	109.03395	109.03533	0.00138
41.04617	109.04561	109.04698	0.00137
41.06179	109.06233	109.06370	0.00137
41.09604	109.09900	109.10035	0.00135
41.51439	109.54729	109.54861	0.00132
41.94728	110.01213	110.01342	0.00129
41.96725	110.03360	110.03489	0.00129
42.00072	110.06958	110.07088	0.00130
42.03380	110.10515	110.10644	0.00129
42.88277	111.02003	111.02131	0.00128
42.93563	111.07712	111.07839	0.00127
42.96938	111.11357	111.11485	0.00128
43.34848	111.52350	111.52478	0.00128
43.77846	111.98936	111.99360	0.00424
43.81354	112.02740	112.02870	0.00130
43.83249	112.04797	112.04926	0.00129
43.86609	112.08441	112.08572	0.00131
43.89840	112.11948	112.12078	0.00130
44.27675	112.53044	112.53176	0.00132
44.70544	112.99698	112.99834	0.00136
44.73957	113.03416	113.03553	0.00137
44.75956	113.05594	113.05731	0.00137
44.82579	113.12813	113.12951	0.00138
45.19866	113.53494	113.53636	0.00142
45.65938	114.03860	114.04010	0.00150
45.68218	114.06357	114.06506	0.00149
46.11717	114.54019	114.54175	0.00156
46.57862	115.04689	115.04853	0.00164
46.60169	115.07225	115.07389	0.00164
47.03191	115.54570	115.54746	0.00176
47.48979	116.05067	116.05254	0.00187
47.87879	116.48056	116.48595	0.00539
48.33895	116.99010	116.99536	0.00526
48.39523	117.05249	117.05774	0.00525
48.40813	117.06680	117.07204	0.00524
48.81813	117.52187	117.52702	0.00515

49.27051	118.02502	118.03005	0.00503
49.28024	118.03586	118.04089	0.00503
49.31157	118.07074	118.07576	0.00502
49.72343	118.52985	118.53478	0.00493
50.13250	118.98672	118.99157	0.00485
50.17258	119.03152	119.03638	0.00486
50.18332	119.04355	119.04839	0.00484
50.21627	119.08038	119.08523	0.00485
50.62240	119.53503	119.53980	0.00477
51.02718	119.98993	119.99373	0.00470
51.07111	120.03835	120.04305	0.00470
51.08404	120.05286	120.05756	0.00470
51.11308	120.08548	120.09017	0.00469
51.51696	120.53949	120.54415	0.00466
51.94646	121.02327	121.02786	0.00459
51.96245	121.04131	121.04589	0.00458
51.97869	121.05962	121.06420	0.00458
52.01071	121.09572	121.10030	0.00458
52.40892	121.54523	121.54979	0.00456
52.83800	122.03055	122.03507	0.00452
52.85732	122.05243	122.05694	0.00451
52.87045	122.06728	122.07183	0.00455
52.90175	122.10274	122.10725	0.00451
53.28519	122.53737	122.54187	0.00450
53.29918	122.55324	122.55774	0.00450
53.72623	123.03824	123.04273	0.00449
53.74624	123.06099	123.06547	0.00448
53.75880	123.07527	123.07976	0.00449
53.78998	123.11072	123.11521	0.00449
54.17028	123.54358	123.54806	0.00448
54.55898	123.98676	123.99360	0.00684
54.59228	124.02478	124.02925	0.00447
54.60960	124.04454	124.04902	0.00448
54.64188	124.08139	124.08588	0.00449
54.67337	124.11734	124.12182	0.00448
55.03301	124.52834	124.53282	0.00448
55.47325	125.03235	125.03686	0.00451
55.49018	125.05174	125.05626	0.00452
55.52289	125.08925	125.09376	0.00451
55.55489	125.12593	125.13045	0.00452
55.90942	125.53270	125.53725	0.00455
56.34889	126.03787	126.04244	0.00457
56.43127	126.13268	126.13726	0.00458
56.78337	126.53830	126.54291	0.00461
57.22167	127.04413	127.04879	0.00466
57.24374	127.06963	127.07703	0.00740
57.30597	127.14154	127.14891	0.00737
57.65391	127.54396	127.55122	0.00726
58.08300	128.04112	128.04826	0.00714
58.09095	128.05034	128.05747	0.00713
58.50818	128.53471	128.54171	0.00700
58.52270	128.55157	128.55858	0.00701
58.95516	129.05461	129.06151	0.00690
58.98212	129.08601	129.09289	0.00688
59.37356	129.54225	129.54903	0.00678
59.38750	129.55850	129.56529	0.00679
59.81335	130.05582	130.06248	0.00666
59.82719	130.07198	130.07864	0.00666

60.21664	130.52763	130.53421	0.00658
60.23524	130.54941	130.55597	0.00656
60.60615	130.98415	130.99063	0.00648
60.64200	131.02620	131.03268	0.00648
60.65444	131.04080	131.04728	0.00648
60.68511	131.07678	131.08325	0.00647
61.07470	131.53436	131.54075	0.00639
61.45974	131.98738	131.99536	0.00798
61.50104	132.03601	132.04232	0.00631
61.51320	132.05032	132.05664	0.00632
61.53177	132.07220	132.07851	0.00631
61.54384	132.08643	132.09273	0.00630
61.92711	132.53830	132.54453	0.00623
62.31756	132.99944	133.00562	0.00618
62.34350	133.03011	133.03628	0.00617
62.35414	133.04269	133.04885	0.00616
62.36669	133.05753	133.06369	0.00616
62.39653	133.09280	133.09897	0.00617
62.77797	133.54424	133.55035	0.00611
63.20206	134.04704	134.05310	0.00606
63.21814	134.06612	134.07217	0.00605
63.24746	134.10092	134.10698	0.00606
63.61184	134.53378	134.53979	0.00601
63.62629	134.55096	134.55697	0.00601
64.03409	135.03627	135.04223	0.00596
64.04698	135.05162	135.05758	0.00596
64.06466	135.07269	135.07864	0.00595
64.09340	135.10692	135.11289	0.00597
64.10073	135.11565	135.12161	0.00596
64.45798	135.54164	135.54757	0.00593
64.47231	135.55875	135.56467	0.00592
64.86150	136.02362	136.02951	0.00589
64.87809	136.04346	136.04935	0.00589
64.89948	136.06902	136.07493	0.00591
64.90907	136.08049	136.08639	0.00590
64.93779	136.11484	136.12072	0.00588
64.94405	136.12233	136.12821	0.00588
65.30064	136.54910	136.55498	0.00588
65.70241	137.03078	137.03662	0.00584
65.71990	137.05177	137.05761	0.00584
65.74968	137.08749	137.09335	0.00586
65.78155	137.12576	137.13160	0.00584
66.11941	137.53160	137.53743	0.00583
66.53954	138.03711	138.04426	0.00715
66.55834	138.05975	138.06690	0.00715
66.58833	138.09589	138.10300	0.00711
66.61787	138.13147	138.13858	0.00711
66.95528	138.53825	138.54524	0.00699
67.37395	139.04387	139.05069	0.00682
67.42391	139.10425	139.11107	0.00682
67.45416	139.14082	139.14764	0.00682
67.78713	139.54373	139.55042	0.00669
68.20319	140.04800	140.05454	0.00654
68.22680	140.07664	140.08318	0.00654
68.28604	140.14853	140.15504	0.00651
68.61747	140.55103	140.55743	0.00640
69.01800	141.03821	141.04449	0.00628
69.03554	141.05957	141.06583	0.00626

69.11519	141.15656	141.16280	0.00624
69.43180	141.54242	141.54858	0.00616
69.44554	141.55917	141.56533	0.00616
69.85087	142.05399	142.06001	0.00602
69.86574	142.07216	142.07817	0.00601
70.23921	142.52885	142.53477	0.00592
70.61135	142.98466	142.99200	0.00734
70.68334	143.07294	143.07872	0.00578
70.70597	143.10069	143.10645	0.00576
71.06048	143.53575	143.54144	0.00569
71.07805	143.55734	143.56301	0.00567
71.46705	144.03554	144.04111	0.00557
71.47914	144.05042	144.05599	0.00557
71.49817	144.07384	144.07939	0.00555
71.50843	144.08646	144.09202	0.00556
71.87667	144.53996	144.54542	0.00546
72.28311	145.04134	145.04671	0.00537
72.29589	145.05711	145.06248	0.00537
72.32639	145.09477	145.10013	0.00536
72.69166	145.54619	145.55146	0.00527
73.09888	146.05028	146.05545	0.00517
73.11285	146.06758	146.07276	0.00518
73.14030	146.10161	146.10677	0.00516
73.50393	146.55255	146.55764	0.00509
73.88466	147.02545	147.03048	0.00503
73.89498	147.03830	147.04356	0.00526
73.91014	147.05714	147.06242	0.00528
73.92449	147.07498	147.08027	0.00529
73.95336	147.11087	147.11617	0.00530
74.30009	147.54234	147.54774	0.00540
74.31494	147.56084	147.56624	0.00540
74.67449	148.00894	148.01447	0.00553
74.72124	148.06728	148.07280	0.00552
74.73410	148.08331	148.08885	0.00554
74.76172	148.11778	148.12332	0.00554
75.10864	148.55096	148.55662	0.00566
75.12282	148.56868	148.57433	0.00565
75.48267	149.01871	149.02448	0.00577
75.51190	149.05530	149.06108	0.00578
75.53000	149.07796	149.08375	0.00579
75.54053	149.09114	149.09693	0.00579
75.56900	149.12679	149.13258	0.00579
76.25276	149.98400	149.99014	0.00605
76.28241	150.02132	150.02737	0.00605
76.30044	150.04396	150.05002	0.00606
76.31452	150.06165	150.06771	0.00606
76.34200	150.09616	150.10223	0.00607
76.37181	150.13362	150.13970	0.00608
76.69579	150.54088	150.54709	0.00621
77.05441	150.99237	150.99823	0.00586
77.07820	151.02234	151.02868	0.00634
77.09777	151.04700	151.05335	0.00635
77.11687	151.07108	151.07742	0.00634
77.14471	151.10616	151.11252	0.00636
77.17387	151.14291	151.14928	0.00637
77.49434	151.54713	151.55363	0.00650
77.89521	152.05353	152.06019	0.00666
77.97149	152.14998	152.15667	0.00669



78.29114	152.55452	152.56133	0.00681
78.68908	153.05890	153.06587	0.00697
78.76767	153.15860	153.16560	0.00700
79.07200	153.54501	153.55215	0.00714
79.08584	153.56261	153.56974	0.00713
79.45925	154.03743	154.04473	0.00730
79.48231	154.06677	154.07409	0.00732
79.56101	154.16695	154.17430	0.00735
79.87724	154.56981	154.57730	0.00749
80.20459	154.98740	154.99503	0.00763
80.24925	155.04442	155.05206	0.00764
80.27745	155.08043	155.08809	0.00766
80.35181	155.17538	155.18308	0.00770
80.63618	155.53883	155.54666	0.00783
81.03757	156.05255	156.06057	0.00802
81.06346	156.08572	156.09375	0.00803
81.42282	156.54643	156.55462	0.00819
81.81295	157.04736	157.05484	0.00748
81.82433	157.06198	157.06945	0.00747
81.84191	157.08458	157.09204	0.00746
81.85236	157.09801	157.10547	0.00746
81.86821	157.11838	157.12584	0.00746
82.20340	157.54950	157.55688	0.00738
82.59507	158.05403	158.06131	0.00728
82.60732	158.06982	158.07710	0.00728
82.63390	158.10410	158.11137	0.00727
82.98497	158.55708	158.56426	0.00718
83.37605	159.06247	159.06956	0.00709
83.38839	159.07843	159.08552	0.00709
83.39692	159.08946	159.09656	0.00710
83.41593	159.11404	159.12113	0.00709
83.76390	159.56447	159.57148	0.00701
84.13875	160.05042	160.05733	0.00691
84.15384	160.06999	160.07691	0.00692
84.16648	160.08638	160.09331	0.00693
84.19294	160.12073	160.12764	0.00691
84.54041	160.57193	160.57877	0.00684
84.89927	161.03860	161.04536	0.00676
84.91384	161.05756	161.06433	0.00677
84.93132	161.08031	161.08707	0.00676
84.94255	161.09492	161.10169	0.00677
84.96979	161.13039	161.13713	0.00674
85.62752	161.98773	161.99040	0.00267
85.67079	162.04422	162.05082	0.00660
85.68668	162.06496	162.07156	0.00660
85.70458	162.08833	162.09492	0.00659
85.71489	162.10179	162.10839	0.00660
85.74208	162.13730	162.14388	0.00658
86.39853	162.99565	163.00212	0.00647
86.42908	163.03566	163.04212	0.00646
86.44309	163.05400	163.06046	0.00646
86.45829	163.07390	163.08036	0.00646
86.51369	163.14647	163.15290	0.00643
87.20714	164.05611	164.06243	0.00632
87.22777	164.08321	164.08951	0.00630
87.28101	164.15315	164.15945	0.00630
87.58890	164.55798	164.56422	0.00624
87.97664	165.06850	165.07467	0.00617

88.02074	165.12660	165.13277	0.00617
88.04813	165.16270	165.16886	0.00616
88.35437	165.56660	165.57270	0.00610
88.73765	166.07280	166.07885	0.00605
88.81104	166.16982	166.17836	0.00854
89.11678	166.57428	166.58265	0.00837
89.46329	167.03328	167.04144	0.00816
89.49754	167.07867	167.08682	0.00815
89.57300	167.17874	167.18684	0.00810
90.23402	168.05650	168.06421	0.00771
90.25550	168.08507	168.09275	0.00768
90.33221	168.18709	168.19473	0.00764
90.93434	168.98898	168.99628	0.00730
90.99377	169.06822	169.07549	0.00727
91.01855	169.10127	169.10852	0.00725
91.08897	169.19522	169.20242	0.00720
91.67118	169.97289	169.97976	0.00687
91.73556	170.05898	170.06583	0.00685
91.76425	170.09735	170.10419	0.00684
91.77342	170.10962	170.11645	0.00683
92.49798	171.08034	171.08675	0.00641
92.49971	171.08266	171.08906	0.00640
92.52543	171.11717	171.12356	0.00639
92.54181	171.13914	171.14553	0.00639
93.16140	171.97157	171.97760	0.00603
93.23950	172.07666	172.08264	0.00598
93.24908	172.08954	172.09553	0.00599
93.98629	173.08301	173.08856	0.00555
93.99424	173.09373	173.09929	0.00556
94.02435	173.13437	173.13990	0.00553
94.70117	174.04912	174.05426	0.00514
94.71564	174.06871	174.07385	0.00514
94.73389	174.09340	174.09854	0.00514
95.44547	175.05789	175.06261	0.00472
95.46125	175.07930	175.08401	0.00471
95.48668	175.11383	175.11853	0.00470
95.51360	175.15038	175.15505	0.00467
96.18504	176.06314	176.06745	0.00431
96.20320	176.08788	176.09217	0.00429
96.25450	176.15771	176.16197	0.00426
96.91972	177.06465	177.06853	0.00388
96.94175	177.09471	177.09859	0.00388
96.99383	177.16582	177.16968	0.00386
97.65962	178.07614	178.08424	0.00810
97.73015	178.17270	178.18076	0.00806
98.39427	179.08334	179.09084	0.00750
98.46619	179.18210	179.18954	0.00744
99.10368	180.05867	180.06560	0.00693
99.12459	180.08746	180.09437	0.00691
99.19844	180.18915	180.19599	0.00684
99.78031	180.99141	180.98880	-0.00261
99.83504	181.06696	181.07329	0.00633
99.85100	181.08899	181.09532	0.00633
99.86119	181.10306	181.10938	0.00632
99.92923	181.19702	181.20329	0.00627
100.50567	181.99402	181.99982	0.00580
100.56319	182.07365	182.07939	0.00574
100.58054	182.09767	182.10341	0.00574

100.58993	182.11067	182.11639	0.00572
100.65809	182.20506	182.21072	0.00566
101.23625	183.00668	183.01188	0.00520
101.31687	183.11861	183.12374	0.00513
101.38488	183.21304	183.21812	0.00508
101.97679	184.03606	184.04063	0.00457
102.00717	184.07834	184.08290	0.00456
102.04013	184.12422	184.12876	0.00454
102.72888	185.08444	185.08842	0.00398
102.74468	185.10651	185.11046	0.00395
102.76404	185.13354	185.13747	0.00393
102.77961	185.15527	185.15920	0.00393
103.37852	185.99245	185.99588	0.00343
104.13803	187.05688	187.05430	-0.00258
104.16844	187.09955	187.09698	-0.00257
104.20487	187.15070	187.14812	-0.00258
104.85365	188.06258	188.06007	-0.00251
104.88582	188.10786	188.10535	-0.00251
105.57154	189.07422	189.07177	-0.00245
105.61058	189.12932	189.12687	-0.00245
105.63687	189.16643	189.16398	-0.00245
106.27891	190.07373	190.07134	-0.00239
106.34888	190.17273	190.17035	-0.00238
106.99088	191.08241	191.08009	-0.00232
107.01091	191.11082	191.10851	-0.00231
107.06121	191.18221	191.17988	-0.00233
107.70086	192.09097	192.08870	-0.00227
107.76973	192.18893	192.18669	-0.00224
108.33332	192.99165	192.98880	-0.00285
108.40731	193.09717	193.09497	-0.00220
108.47784	193.19778	193.19558	-0.00220
109.09204	194.07497	194.07283	-0.00214
109.11051	194.10138	194.09924	-0.00214
109.18338	194.20560	194.20345	-0.00215
109.79687	195.08408	195.08200	-0.00208
109.81186	195.10558	195.10349	-0.00209
109.82131	195.11913	195.11703	-0.00210
109.88680	195.21303	195.21094	-0.00209
110.48961	196.07846	196.07643	-0.00203
110.50219	196.09656	196.09452	-0.00204
110.51865	196.12021	196.11818	-0.00203
110.58870	196.22092	196.21889	-0.00203
111.17309	197.06206	197.05978	-0.00228
111.19127	197.08824	197.08598	-0.00226
111.22212	197.13272	197.13044	-0.00228
111.28896	197.22905	197.22678	-0.00227
111.85777	198.04987	198.04768	-0.00219
111.87096	198.06892	198.06674	-0.00218
111.88842	198.09415	198.09196	-0.00219
112.55461	199.05779	199.05568	-0.00211
112.58385	199.10013	199.09803	-0.00210
112.63239	199.17046	199.16835	-0.00211
113.24996	200.06613	200.06410	-0.00203
113.27857	200.10767	200.10566	-0.00201
113.89007	200.99664	200.99503	-0.00161
113.94024	201.06966	201.06772	-0.00194
113.97235	201.11642	201.11448	-0.00194
114.00629	201.16583	201.16388	-0.00195

114.63226	202.07828	202.07642	-0.00186
114.66362	202.12405	202.12218	-0.00187
115.31915	203.08197	203.08016	-0.00181
115.36124	203.14352	203.14174	-0.00178
115.38684	203.18100	203.17920	-0.00180
116.00534	204.08711	204.08537	-0.00174
116.07400	204.18782	204.18610	-0.00172
116.62026	204.98999	204.98831	-0.00168
116.67696	205.07335	205.07168	-0.00167
116.69176	205.09511	205.09344	-0.00167
116.76053	205.19623	205.19457	-0.00166
117.36943	206.09274	206.09112	-0.00162
117.38257	206.11209	206.11049	-0.00160
117.44432	206.20314	206.20152	-0.00162
118.04078	207.08347	207.08189	-0.00158
118.05789	207.10873	207.10718	-0.00155
118.12768	207.21187	207.21033	-0.00154
118.71676	208.08345	208.08194	-0.00151
118.73749	208.11415	208.11264	-0.00151
118.80798	208.21858	208.21708	-0.00150
119.39412	209.08794	209.08665	-0.00129
119.41896	209.12480	209.12354	-0.00126
119.48781	209.22705	209.22579	-0.00126
120.06820	210.08997	210.08876	-0.00121
120.08475	210.11459	210.11340	-0.00119
120.16606	210.23564	210.23446	-0.00118
120.71809	211.05835	211.05721	-0.00114
120.73053	211.07690	211.07577	-0.00113
120.74534	211.09900	211.09788	-0.00112
120.84195	211.24316	211.24205	-0.00111
121.34101	211.98866	211.98720	-0.00146
121.39578	212.07056	212.06949	-0.00107
121.40820	212.08913	212.08807	-0.00106
121.42063	212.10773	212.10665	-0.00108
122.01380	212.99577	212.99477	-0.00100
122.06535	213.07303	213.07204	-0.00099
122.09376	213.11562	213.11462	-0.00100
122.12657	213.16483	213.16382	-0.00101
122.14104	213.18652	213.18551	-0.00101
122.73191	214.07338	214.07245	-0.00093
122.76212	214.11879	214.11784	-0.00095
123.40378	215.08411	215.08322	-0.00089
123.46780	215.18054	215.17965	-0.00089
124.06971	216.08829	216.08743	-0.00086
124.66664	216.99042	216.98913	-0.00129
124.73472	217.09343	217.09214	-0.00129
124.77772	217.15849	217.15722	-0.00127
124.80296	217.19669	217.19542	-0.00127
125.38237	218.07460	218.07342	-0.00118
125.40072	218.10243	218.10125	-0.00118
125.44452	218.16887	218.16771	-0.00116
125.46832	218.20499	218.20381	-0.00118
125.98355	218.98737	218.98629	-0.00108
126.04014	219.07339	219.07231	-0.00108
126.06132	219.10559	219.10452	-0.00107
126.13170	219.21260	219.21154	-0.00106
126.69977	220.07735	220.07636	-0.00099
126.72421	220.11458	220.11360	-0.00098

126.79294	220.21933	220.21835	-0.00098
127.36269	221.08862	221.08773	-0.00089
127.38476	221.12234	221.12145	-0.00089
127.45400	221.22812	221.22722	-0.00090
128.02016	222.09393	222.09312	-0.00081
128.03930	222.12325	222.12241	-0.00084
128.11290	222.23593	222.23512	-0.00081
128.67644	223.09972	223.09898	-0.00074
128.70239	223.13954	223.13879	-0.00075
128.76956	223.24261	223.24188	-0.00073
129.25524	223.98868	223.98720	-0.00148
129.30451	224.06442	224.06374	-0.00068
129.33000	224.10362	224.10294	-0.00068
129.35100	224.13591	224.13523	-0.00068
129.36449	224.15666	224.15599	-0.00067
129.42612	224.25146	224.25078	-0.00068
129.90968	224.99596	224.99533	-0.00063
129.96140	225.07567	225.07504	-0.00063
129.98614	225.11380	225.11316	-0.00064
130.07994	225.25839	225.25778	-0.00061
130.61200	226.07948	226.07891	-0.00057
130.63584	226.11630	226.11573	-0.00057
131.26089	227.08292	227.08239	-0.00053
131.29278	227.13229	227.13176	-0.00053
131.91009	228.08910	228.08858	-0.00052
131.98692	228.20831	228.20745	-0.00086
132.55653	229.09323	229.09246	-0.00077
132.62247	229.19577	229.19501	-0.00076
133.19073	230.08052	230.07985	-0.00067
133.20642	230.10498	230.10432	-0.00066
133.77103	230.98579	230.98560	-0.00019
133.83272	231.08214	231.08158	-0.00056
133.84929	231.10803	231.10746	-0.00057
133.91521	231.21100	231.21044	-0.00056
134.41314	231.98959	231.98911	-0.00048
134.47144	232.08083	232.08038	-0.00045
134.49242	232.11368	232.11322	-0.00046
134.55912	232.21811	232.21765	-0.00046
135.05895	233.00139	233.00102	-0.00037
135.11278	233.08583	233.08545	-0.00038
135.13402	233.11916	233.11879	-0.00037
135.20286	233.22717	233.22681	-0.00036
135.72575	234.04843	234.04813	-0.00030
135.74949	234.08575	234.08546	-0.00029
135.77091	234.11943	234.11914	-0.00029
135.84309	234.23293	234.23265	-0.00028
136.36714	235.05780	235.05758	-0.00022
136.39294	235.09845	235.09824	-0.00021
136.41676	235.13599	235.13577	-0.00022
136.48413	235.24216	235.24195	-0.00021
136.95643	235.98714	235.98697	-0.00017
137.00525	236.06421	236.06404	-0.00017
137.03271	236.10757	236.10741	-0.00016
137.04928	236.13374	236.13358	-0.00016
137.06260	236.15477	236.15461	-0.00016
137.09982	236.21355	236.21339	-0.00016
137.12237	236.24916	236.24901	-0.00015
137.64248	237.07141	237.07128	-0.00013

137.66916	237.11363	237.11351	-0.00012
137.69547	237.15526	237.15514	-0.00012
137.75935	237.25636	237.25627	-0.00009
138.27402	238.07175	238.07167	-0.00008
138.30163	238.11552	238.11543	-0.00009
138.39578	238.26486	238.26477	-0.00009
138.91400	239.08765	239.08763	-0.00002
138.94072	239.13010	239.13009	-0.00001
139.03011	239.27220	239.27218	-0.00002
139.54171	240.08618	240.08625	0.00007
139.56633	240.12541	240.12546	0.00005
140.17431	241.09467	241.09480	0.00013
140.80014	242.09442	242.09464	0.00022
141.35738	242.98642	242.98560	-0.00082
141.41011	243.07091	243.07114	0.00023
141.43229	243.10645	243.10669	0.00024
141.98315	243.99007	243.99035	0.00028
142.04241	244.08522	244.08551	0.00029
142.06140	244.11572	244.11600	0.00028
142.66716	245.08952	245.08985	0.00033
142.68752	245.12230	245.12261	0.00031
142.75195	245.22600	245.22632	0.00032
143.28884	246.09097	246.09133	0.00036
143.30856	246.12279	246.12313	0.00034
143.90204	247.08080	247.08117	0.00037
143.91713	247.10518	247.10475	-0.00043
143.93651	247.13651	247.13606	-0.00045
144.00181	247.24203	247.24162	-0.00041
144.53050	248.09735	248.09703	-0.00032
144.55510	248.13718	248.13686	-0.00032
144.62399	248.24875	248.24845	-0.00030
145.13541	249.07780	249.07758	-0.00022
145.15887	249.11586	249.11565	-0.00021
145.18023	249.15053	249.15031	-0.00022
145.24654	249.25813	249.25794	-0.00019
145.75089	250.07741	250.07728	-0.00013
145.77561	250.11760	250.11747	-0.00013
145.79491	250.14897	250.14886	-0.00011
145.86620	250.26491	250.26480	-0.00011
146.36777	251.08138	251.08128	-0.00010
146.39756	251.12990	251.12983	-0.00007
146.48521	251.27272	251.27266	-0.00006
146.98732	252.09169	252.09167	-0.00002
147.01219	252.13229	252.13228	-0.00001
147.10372	252.28172	252.28173	0.00001
147.60216	253.09636	253.09641	0.00005
147.63344	253.14752	253.14759	0.00007
147.71960	253.28848	253.28856	0.00008
148.21558	254.10072	254.10084	0.00012
148.75508	254.98573	254.98588	0.00015
148.82483	255.10028	255.10043	0.00015
148.89209	255.21075	255.21090	0.00015
149.42013	256.07886	256.07904	0.00018
149.44136	256.11377	256.11397	0.00020
149.41832	256.24023	256.24064	0.00041
150.03114	257.08521	257.08545	0.00024
150.05197	257.11938	257.11979	0.00041
150.12820	257.24512	257.24551	0.00039

150.64123	258.09204	258.09233	0.00029
150.66152	258.12549	258.12584	0.00035
151.23004	259.06567	259.06598	0.00031
151.25130	259.10083	259.10117	0.00034
151.27273	259.13623	259.13663	0.00040
151.33685	259.24243	259.24280	0.00037
151.85732	260.10498	260.10527	0.00029
151.87824	260.13965	260.13997	0.00032
151.94427	260.24927	260.24949	0.00022
152.44163	261.07495	261.07527	0.00032
152.46734	261.11768	261.11798	0.00030
152.55189	261.25830	261.25851	0.00021
153.05318	262.09229	262.09243	0.00014
153.07318	262.12549	262.12576	0.00027
153.08927	262.15234	262.15257	0.00023
153.15736	262.26563	262.26596	0.00033
153.59322	262.99219	262.99183	0.00036
153.65289	263.09155	263.09194	0.00039
153.67778	263.13330	263.13346	0.00016
153.69717	263.16553	263.16580	0.00027
153.76204	263.27368	263.27405	0.00037
154.24859	264.08643	264.08661	0.00018
154.27514	264.13086	264.13099	0.00013
154.34363	264.24536	264.24549	0.00013
154.85327	265.09790	265.09824	0.00034
154.88266	265.14722	265.14745	0.00023
155.45171	266.10107	266.10134	0.00027
155.47977	266.14819	266.14842	0.00023
155.56876	266.29761	266.29776	0.00015
155.97882	266.98633	266.98647	0.00014
156.05155	267.10864	267.10872	0.00008
156.08398	267.16309	267.16323	0.00014
156.16849	267.30518	267.30531	0.00013
156.64670	268.11011	268.11010	0.00001
157.16524	268.98413	268.98413	0.0
157.22537	269.08569	269.08557	0.00012
157.24653	269.12134	269.12127	0.00007
157.80555	270.06543	270.06539	0.00004
157.81916	270.08862	270.08839	0.00023
157.84355	270.12988	270.12963	0.00025
158.40045	271.07227	271.07194	0.00033
158.41719	271.10059	271.10028	0.00031
158.43917	271.13770	271.13751	0.00019
158.99199	272.07495	272.07468	0.00027
159.01124	272.10767	272.10678	0.00089
159.03090	272.14111	272.14015	0.00096
159.57225	273.06055	273.05969	0.00086
159.58567	273.08350	273.08250	0.00100
159.60570	273.11743	273.11657	0.00086
159.62617	273.15234	273.15137	0.00097
159.68882	273.25879	273.25790	0.00089
160.17748	274.09058	274.08960	0.00098
160.19810	274.12573	274.12473	0.00100
160.21474	274.15405	274.15307	0.00098
160.75356	275.07275	275.07174	0.00101
160.76587	275.09375	275.09274	0.00101
160.78820	275.13184	275.13084	0.00100
160.80956	275.16821	275.16728	0.00093

160.87173	275.27441	275.27342	-0.00099
161.35202	276.09497	276.09389	-0.00108
161.37499	276.13428	276.13316	-0.00112
161.39550	276.16919	276.16822	-0.00097
161.93236	277.08789	277.08693	-0.00096
161.94813	277.11499	277.11394	-0.00105
161.96755	277.14819	277.14720	-0.00099
162.05078	277.29077	277.28977	-0.00100
162.52403	278.10229	278.10119	-0.00110
162.55313	278.15234	278.15114	-0.00120
162.63779	278.29761	278.29643	-0.00118
163.10693	279.10352	279.10228	-0.00124
163.12696	279.13794	279.13671	-0.00123
163.14098	279.16211	279.16082	-0.00129
163.67764	280.08545	280.08416	-0.00129
163.69626	280.11768	280.11624	-0.00144
163.72311	280.16382	280.16247	-0.00135
163.76826	280.24170	280.24025	-0.00145
163.80982	280.31323	280.31184	-0.00139
164.19974	280.98535	280.98239	-0.00296
164.27712	281.11890	281.11744	-0.00146
164.84271	282.09570	282.09407	-0.00163
164.86263	282.13013	282.12849	-0.00164
165.42493	283.10303	283.10119	-0.00184
165.44628	283.13989	283.13815	-0.00174
165.99070	284.08350	284.08159	-0.00191
166.00382	284.10620	284.10215	-0.00405
166.02629	284.14526	284.14113	-0.00413
166.10113	284.27515	284.27099	-0.00416
166.56781	285.08545	285.08141	-0.00404
166.58691	285.11865	285.11461	-0.00404
166.60834	285.15601	285.15185	-0.00416
166.67967	285.28003	285.27584	-0.00419
167.08651	285.98755	285.98354	-0.00401
167.13731	286.07617	286.07197	-0.00420
167.16744	286.12842	286.12444	-0.00398
167.18518	286.15942	286.15533	-0.00409
167.71567	287.08374	287.07974	-0.00400
167.74608	287.13696	287.13277	-0.00419
168.28901	288.08472	288.08050	-0.00422
168.31588	288.13159	288.12745	-0.00414
168.33779	288.16992	288.16573	-0.00419
168.87387	289.10742	289.10321	-0.00421
168.90012	289.15332	289.14915	-0.00417
168.98010	289.29321	289.28914	-0.00407
169.45081	290.11792	290.11383	-0.00409
170.01427	291.10693	291.10258	-0.00435
170.03010	291.13477	291.13038	-0.00439
170.04861	291.16724	291.16289	-0.00435
170.12996	291.31006	291.30586	-0.00420
170.58943	292.11792	292.11359	-0.00433
170.61621	292.16504	292.16073	-0.00431
170.70238	292.31665	292.31236	-0.00429
171.08379	292.98853	292.98239	-0.00614
171.14142	293.09009	293.08556	-0.00453
171.16183	293.12598	293.12154	-0.00444
171.19625	293.18677	293.18220	-0.00457
171.70110	294.07739	294.07273	-0.00466



171.73218	294.13232	294.12760	-0.00472
172.26772	295.07861	295.07386	-0.00475
172.28495	295.10913	295.10432	-0.00481
172.30511	295.14478	295.13997	-0.00481
172.85573	296.11963	296.11457	-0.00506
172.87427	296.15234	296.14742	-0.00492
173.42180	297.12329	297.11822	-0.00507
173.44316	297.16113	297.15612	-0.00501
173.98334	298.12085	298.11551	-0.00534
174.00732	298.16357	298.15815	-0.00542
174.52450	299.08374	299.07822	-0.00552
174.53798	299.10767	299.10222	-0.00545
174.55617	299.14014	299.13461	-0.00553
174.57558	299.17480	299.16918	-0.00562
175.09372	300.09839	300.09254	-0.00585
175.11953	300.14429	300.13720	-0.00709
175.13755	300.17651	300.16935	-0.00716
175.65846	301.10669	301.09963	-0.00706
175.68626	301.15625	301.14931	-0.00694
175.70517	301.19019	301.18312	-0.00707
176.21817	302.10840	302.10151	-0.00689
176.24269	302.15161	302.14471	-0.00690
176.78422	303.12183	303.11507	-0.00676
176.81158	303.17090	303.16415	-0.00675
176.89050	303.31226	303.30569	-0.00657
177.34333	304.12524	304.11856	-0.00668
177.36736	304.16821	304.16172	-0.00649
177.82454	304.98999	304.98240	-0.00759
177.90205	305.12939	305.12302	-0.00637
177.93321	305.18555	305.17910	-0.00645
178.01193	305.32715	305.32076	-0.00639
178.45712	306.12891	306.12259	-0.00632
178.98525	307.08154	307.07517	-0.00637
178.99945	307.10718	307.10080	-0.00638
179.01934	307.14307	307.13670	-0.00637
179.54604	308.09448	308.08828	-0.00620
179.57437	308.14575	308.13952	-0.00623
180.09781	309.09302	309.08677	-0.00625
180.11388	309.12207	309.11587	-0.00620
180.13373	309.15796	309.15182	-0.00614
180.63704	310.07031	310.06414	-0.00617
180.67343	310.13647	310.13013	-0.00634
180.68934	310.16528	310.15901	-0.00627
181.20480	311.10107	311.09489	-0.00618
181.22593	311.13940	311.13329	-0.00611
181.24616	311.17627	311.17004	-0.00623
181.77597	312.13989	312.13356	-0.00633
181.79744	312.17896	312.17204	-0.00892
182.31360	313.11914	313.11274	-0.00840
182.33661	313.16113	313.15271	-0.00842
182.35460	313.19385	313.18553	-0.00832
182.85907	314.11450	314.10640	-0.00810
182.87679	314.14673	314.13878	-0.00795
182.88731	314.16602	314.15799	-0.00803
182.90204	314.19287	314.18492	-0.00795
183.41401	315.12866	315.12099	-0.00767
183.44120	315.17822	315.17076	-0.00746
183.96276	316.13306	316.12588	-0.00718

183.98640	316.17627	316.16922	-0.00705
184.43402	316.99707	316.99017	-0.00690
184.51241	317.14087	317.13406	-0.00681
184.54109	317.19336	317.18671	-0.00665
185.05860	318.14380	318.13747	-0.00633
185.52001	318.99243	318.97920	-0.01323
185.60345	319.14624	319.14004	-0.00620
186.15097	320.15479	320.14910	-0.00569
186.67733	321.12622	321.12070	-0.00552
186.69717	321.16284	321.15735	-0.00549
187.21258	322.11548	322.11023	-0.00525
187.23965	322.16553	322.16031	-0.00522
187.75024	323.11060	323.10577	-0.00483
187.76672	323.14136	323.13630	-0.00506
187.78558	323.17627	323.17125	-0.00502
188.27860	324.09033	324.08559	-0.00474
188.29868	324.12744	324.11754	-0.00990
188.30979	324.14819	324.13819	-0.01000
188.32528	324.17700	324.16695	-0.01005
188.85217	325.15552	325.14621	-0.00931
188.87145	325.19116	325.18207	-0.00909
189.37065	326.11987	326.11129	-0.00858
189.39052	326.15674	326.14829	-0.00845
189.40892	326.19092	326.18259	-0.00833
189.90998	327.12451	327.11670	-0.00781
189.93481	327.17090	327.16303	-0.00787
190.44554	328.12378	328.11665	-0.00713
190.46851	328.16650	328.15956	-0.00694
190.98675	329.13501	329.12871	-0.00630
191.01336	329.18481	329.17851	-0.00630
191.52239	330.13770	330.13190	-0.00580
191.97463	330.98535	330.97919	-0.00616
192.05955	331.14453	331.13949	-0.00504
192.59369	332.14746	332.14295	-0.00451
193.11068	333.11963	333.11565	-0.00398
193.13009	333.15601	333.15218	-0.00383
193.64696	334.12939	334.12615	-0.00324
193.66329	334.16016	334.15696	-0.00320
194.18021	335.13525	335.13248	-0.00277
194.19925	335.17114	335.16846	-0.00268
194.70000	336.11719	336.11489	-0.00230
194.71225	336.14014	336.13807	-0.00207
194.72864	336.17114	336.16906	-0.00208
195.24626	337.15063	337.14890	-0.00173
195.26455	337.18530	337.18244	-0.00286
195.77375	338.15015	338.14798	-0.00217
195.79192	338.18457	338.18246	-0.00211
196.28827	339.12646	339.12503	-0.00143
196.32643	339.19897	339.19754	-0.00143
196.81265	340.12305	340.12226	-0.00079
196.83289	340.16162	340.16077	-0.00085
197.33952	341.12573	341.12572	-0.00001
197.86568	342.12891	342.12932	0.00041
198.31113	342.97900	342.97919	0.00019
198.39289	343.13501	343.13641	0.00140
198.92097	344.14478	344.14667	0.00189
199.44702	345.15210	345.15453	0.00243
199.96961	346.15430	346.15723	0.00293

200.49634	347.16577	347.16937	0.00360
201.01692	348.16724	348.17116	0.00392
201.52474	349.14526	349.14981	0.00455
201.54290	349.18066	349.18343	0.00277
202.56812	351.15942	351.16386	0.00444
203.60805	353.17310	353.17849	0.00539
204.53588	354.97461	354.97919	0.00458
206.68214	359.15967	359.16784	0.00817
207.70994	361.17285	361.18169	0.00884
210.65289	366.96899	366.97920	0.01021
211.66067	368.96460	368.97509	0.01049
217.66172	380.96387	380.97600	0.01213
223.56862	392.96777	392.97599	0.00822
225.22560	396.36938	396.37558	0.00620

01	0.3011E 01	0.3011E 01	0.
01	0.3011E 01	0.3011E 01	0.
01	0.3011E 01	0.3011E 01	0.
01	0.3011E 01	0.3011E 01	0.

TABLE 2.3 - FINAL DATA OUTPUT FOR SPECTRUM G

<u>reference distances</u>	<u>reference masses</u>		
17.12426	84.96565		
61.43302	131.99536		
99.75703	180.98880		
141.33971	242.98560		
177.81491	304.98240		
5			
0.1946E-04	0.2286E-04	0.2135E-04	0.2445E-04
0.1977E-04	0.2317E-04	0.2144E-04	0.2454E-04
0.1879E 01	0.3411E 01	0.4316E 01	0.6629E 01
0.2940E 01	0.4689E 01	0.5806E 01	0.8329E 01

<u>distance</u>	<u>mass M<sub>1</sub></u>	<u>mass M<sub>2</sub></u>	<u>M<sub>2</sub> - M<sub>1</sub></u>
17.19157	85.02933	85.03163	0.00230
17.22971	85.06543	85.06766	0.00223
17.26811	85.10181	85.10396	0.00215
18.23234	86.01726	86.01771	0.00045
18.25446	86.03833	86.03874	0.00041
18.29268	86.07472	86.07506	0.00034
18.32629	86.10672	86.10702	0.00030
19.28908	87.02609	87.02481	-0.00128
19.31081	87.04689	87.04557	-0.00132
19.81440	87.52974	87.52765	-0.00209
20.33961	88.03473	88.03185	-0.00288
20.36119	88.05550	88.05260	-0.00290
20.86008	88.53654	88.53294	-0.00360
21.38283	89.04198	89.03767	-0.00431
21.89975	89.54317	89.53819	-0.00498
22.42060	90.04958	90.04397	-0.00561
23.44269	91.04741	91.04064	-0.00677
23.45736	91.06177	91.05498	-0.00679
24.44695	92.03311	92.02532	-0.00779
24.48137	92.06699	92.05916	-0.00783
25.42979	93.00284	92.99520	-0.00764
25.46798	93.04062	93.03193	-0.00869
25.50484	93.07710	93.06838	-0.00872
25.96754	93.53555	93.52645	-0.00910
26.47369	94.03831	94.02884	-0.00947
26.48680	94.05136	94.04188	-0.00948
26.52096	94.08534	94.07584	-0.00950
26.98019	94.54277	94.53295	-0.00982
27.45750	95.01936	95.00924	-0.01012
27.48429	95.04614	95.03601	-0.01013
27.49598	95.05783	95.04770	-0.01013
27.53228	95.09413	95.08397	-0.01016
27.98383	95.54628	95.53586	-0.01042
28.48873	96.05309	96.04241	-0.01068
28.50245	96.06688	96.05619	-0.01069
28.53672	96.10133	96.09062	-0.01071
28.98587	96.55341	96.54249	-0.01092
29.47297	97.04486	97.03376	-0.01110
29.48558	97.05760	97.04649	-0.01111
29.53738	97.10994	97.09882	-0.01112
30.44067	98.02489	98.01346	-0.01143
30.49651	98.08159	98.07251	-0.00908
30.53143	98.11705	98.10791	-0.00914
31.43143	99.03329	99.02351	-0.00978
31.45171	99.05399	99.04419	-0.00980
31.48698	99.09000	99.08016	-0.00984
31.52279	99.12656	99.11668	-0.00988
31.92400	99.53654	99.52641	-0.01013
32.37977	100.00331	99.99289	-0.01042
32.41668	100.04117	100.03071	-0.01046
32.43687	100.06187	100.05141	-0.01046
32.47227	100.09819	100.08770	-0.01049
32.50340	100.13013	100.11962	-0.01051
32.90571	100.54330	100.53256	-0.01074
33.35988	101.01076	101.00143	-0.00933
33.39568	101.04764	101.03663	-0.01101
33.41780	101.07043	101.05942	-0.01101
33.88144	101.54889	101.53763	-0.01126

34.36836	102.05255	102.04110	-0.01145
34.85080	102.55283	102.54116	-0.01167
35.32983	103.05074	103.03891	-0.01183
35.34318	103.06464	103.05279	-0.01185
36.27404	104.03568	104.02358	-0.01210
36.29472	104.05730	104.04520	-0.01210
36.30877	104.07201	104.05989	-0.01212
37.23403	105.04184	105.02956	-0.01228
37.27042	105.08009	105.06779	-0.01230
37.70441	105.53659	105.52426	-0.01233
38.18156	106.03966	106.02728	-0.01238
38.19189	106.05055	106.03818	-0.01237
38.21680	106.07686	106.06448	-0.01238
38.22807	106.08876	106.07638	-0.01238
38.56745	106.54257	106.53017	-0.01240
38.66416	106.54967	106.53727	-0.01240
39.13251	107.04578	107.03339	-0.01239
39.14584	107.05992	107.04753	-0.01239
39.17845	107.09450	107.08211	-0.01239
39.60612	107.54863	107.53626	-0.01237
40.08061	108.05357	108.04126	-0.01231
40.09393	108.06776	108.05776	-0.01000
40.12602	108.10197	108.09195	-0.01002
40.54937	108.55360	108.54346	-0.01014
41.00819	109.04410	109.03389	-0.01021
41.01945	109.05617	109.04594	-0.01023
41.03581	109.07367	109.06344	-0.01023
41.07015	109.11043	109.10020	-0.01023
41.48789	109.55812	109.54782	-0.01030
41.92167	110.02396	110.01360	-0.01036
41.94291	110.04680	110.03643	-0.01037
41.97436	110.08061	110.07025	-0.01036
42.00779	110.11656	110.10620	-0.01036
42.41043	110.55003	110.53963	-0.01040
42.85719	111.03198	111.02155	-0.01043
42.87598	111.05228	111.04184	-0.01044
42.90966	111.08864	111.07822	-0.01042
42.94328	111.12495	111.11454	-0.01041
43.32263	111.53519	111.52475	-0.01044
43.75234	112.00076	111.99360	-0.00716
43.78804	112.03949	112.02907	-0.01042
43.80631	112.05931	112.04889	-0.01042
43.83996	112.09581	112.08540	-0.01041
43.87247	112.13110	112.12068	-0.01042
44.25088	112.54213	112.53175	-0.01038
44.67956	113.00868	112.99833	-0.01035
44.71362	113.04579	113.03545	-0.01034
44.73378	113.06776	113.05741	-0.01035
44.79991	113.13983	113.12950	-0.01033
45.17306	113.54695	113.53667	-0.01028
45.63358	114.05042	114.04021	-0.01021
45.65624	114.07521	114.06502	-0.01019
46.09135	114.55196	114.54186	-0.01010
46.55241	115.05821	115.04823	-0.00998
46.57596	115.08411	115.07413	-0.00998
46.99621	115.54657	115.53671	-0.00986
47.00764	115.55917	115.54930	-0.00987
47.45886	116.05676	116.04705	-0.00971

47.47148	116,07071	116,06486	-0,00585
47.48916	116,09023	116,08439	-0,00584
47.90369	116,54837	116,54242	-0,00595
47.91706	116,56316	116,55721	-0,00595
48.31297	117,00159	116,99555	-0,00604
48.33828	117,02965	117,02360	-0,00605
48.34757	117,03995	117,03389	-0,00606
48.35696	117,05035	117,04430	-0,00605
48.36877	117,06345	117,05739	-0,00606
48.38029	117,07623	117,07016	-0,00607
48.38679	117,08344	117,07737	-0,00607
48.79266	117,53391	117,52775	-0,00616
48.81239	117,55583	117,54966	-0,00617
49.24329	118,03506	118,02883	-0,00623
49.25433	118,04736	118,04112	-0,00624
49.27463	118,06996	118,06372	-0,00624
49.28730	118,08406	118,07782	-0,00624
49.69795	118,54179	118,53548	-0,00631
49.71879	118,56503	118,55873	-0,00630
50.10623	118,99773	118,99139	-0,00634
50.14602	119,04221	119,03586	-0,00635
50.15797	119,05557	119,04922	-0,00635
50.19023	119,09164	119,08530	-0,00634
50.59669	119,54662	119,54022	-0,00640
51.00158	120,00067	119,99426	-0,00641
51.04486	120,04927	120,04285	-0,00642
51.05785	120,06384	120,05743	-0,00641
51.08346	120,09261	120,08618	-0,00643
51.09198	120,10217	120,09576	-0,00641
51.49093	120,55060	120,54418	-0,00642
51.92033	121,03419	121,02777	-0,00642
51.93686	121,05283	121,04640	-0,00643
51.95338	121,07146	121,06503	-0,00643
51.97472	121,09552	121,08909	-0,00643
51.98580	121,10802	121,10159	-0,00643
52.38247	121,55574	121,54932	-0,00642
52.79448	122,02165	122,01525	-0,00640
52.81219	122,04170	122,03531	-0,00639
52.83160	122,06367	122,05728	-0,00639
52.84570	122,07964	122,07325	-0,00639
52.87568	122,11359	122,10719	-0,00640
53.25986	122,54900	122,54263	-0,00637
53.27343	122,56439	122,55802	-0,00637
53.68133	123,02756	123,02124	-0,00632
53.70049	123,04933	123,04302	-0,00631
53.72035	123,07190	123,06559	-0,00631
53.73244	123,08565	123,07934	-0,00631
53.76396	123,12149	123,11518	-0,00631
54.12402	123,53120	123,52495	-0,00625
54.14423	123,55423	123,54797	-0,00626
54.53335	123,99782	123,99360	-0,00422
54.56652	124,03568	124,02950	-0,00618
54.58365	124,05522	124,04905	-0,00617
54.61604	124,09219	124,08602	-0,00617
54.64721	124,12778	124,12161	-0,00617
55.00722	124,53911	124,53301	-0,00610
55.02653	124,56119	124,55510	-0,00609
55.44768	125,04329	125,03728	-0,00601

55.46561	125,06383	125,05784	-0,00599
55.49694	125,09973	125,09376	-0,00597
55.52900	125,13647	125,13050	-0,00597
55.88356	125,54321	125,53734	-0,00587
56.32349	126,04881	126,04305	-0,00576
56.34396	126,07236	126,06661	-0,00575
56.40550	126,14317	126,13743	-0,00574
56.75797	126,54913	126,54350	-0,00563
57.19566	127,05415	127,04867	-0,00548
57.21805	127,08002	127,07741	-0,00261
57.28008	127,15167	127,14906	-0,00261
57.62643	127,55217	127,54951	-0,00266
58.05795	128,05203	128,04934	-0,00269
58.07334	128,06989	128,06718	-0,00271
58.08837	128,08731	128,08462	-0,00269
58.48264	128,54495	128,54222	-0,00273
58.49667	128,56125	128,55851	-0,00274
58.92854	129,06349	129,06074	-0,00275
58.95598	129,09543	129,09268	-0,00275
59.32905	129,53014	129,52737	-0,00277
59.34821	129,55247	129,54972	-0,00275
59.36169	129,56821	129,56544	-0,00277
59.75906	130,03209	130,02932	-0,00277
59.78937	130,06750	130,06475	-0,00275
59.80172	130,08194	130,07918	-0,00276
60.19125	130,53757	130,53482	-0,00275
60.20979	130,55928	130,55652	-0,00276
60.58004	130,99313	130,99039	-0,00274
60.61819	131,03787	131,03514	-0,00273
60.63015	131,05191	131,04917	-0,00274
60.65061	131,07590	131,07317	-0,00273
60.66200	131,08926	131,08653	-0,00273
61.04880	131,54344	131,54073	-0,00271
61.06875	131,56689	131,56419	-0,00270
61.43780	132,00098	131,99833	-0,00265
61.47486	132,04462	132,04196	-0,00266
61.48450	132,05597	132,05685	0,00088
61.50707	132,08253	132,07989	-0,00264
61.51856	132,09607	132,09342	-0,00265
61.90146	132,54738	132,54479	-0,00259
62.29208	133,00861	133,00605	-0,00256
62.31568	133,03050	133,03394	-0,00256
62.32888	133,05211	133,04954	-0,00257
62.34182	133,06740	133,06484	-0,00256
62.75084	133,55130	133,54881	-0,00249
63.17531	134,05441	134,05198	-0,00243
63.19227	134,07454	134,07211	-0,00243
63.22119	134,10886	134,10643	-0,00243
63.58708	134,54338	134,54103	-0,00235
63.60077	134,55966	134,55731	-0,00235
63.99040	135,02319	135,02091	-0,00228
64.00780	135,04391	135,04164	-0,00227
64.02093	135,05954	135,05728	-0,00226
64.03936	135,08148	135,07923	-0,00225
64.06941	135,11728	135,11502	-0,00226
64.43223	135,54977	135,54760	-0,00217
64.44629	135,56654	135,56437	-0,00217
64.83543	136,03123	136,02915	-0,00208



64.85211	136,05116	136,04908	-0,00208
64.87343	136,07664	136,07457	-0,00207
64.88345	136,08862	136,08655	-0,00207
64.91313	136,12411	136,12203	-0,00208
65.25608	136,53442	136,53244	-0,00198
65.27533	136,55746	136,55550	-0,00196
65.67684	137,03868	137,03682	-0,00186
65.69414	137,05943	137,05757	-0,00186
65.71313	137,08221	137,08037	-0,00184
65.72457	137,09595	137,09410	-0,00185
65.75477	137,13217	137,13033	-0,00184
66.09454	137,54021	137,53845	-0,00176
66.11514	137,56497	137,56520	0,00023
66.51407	138,04483	138,04503	0,00020
66.53290	138,06750	138,06771	0,00021
66.56255	138,10321	138,10340	0,00019
66.59234	138,13910	138,13928	0,00018
66.93024	138,54636	138,54649	0,00013
67.34846	139,05124	139,05135	0,00011
67.37225	139,07999	139,08010	0,00011
67.39814	139,11128	139,11138	0,00010
67.42832	139,14777	139,14786	0,00009
67.75944	139,54831	139,54837	0,00006
68.17702	140,05426	140,05429	0,00003
68.20139	140,08382	140,08384	0,00002
68.26025	140,15520	140,15524	0,00004
68.58178	140,54555	140,54556	0,00001
68.59431	140,56076	140,56078	0,00002
69.00931	141,06541	141,06541	0,0
69.03500	141,09669	141,09667	-0,00002
69.08947	141,16299	141,16298	-0,00001
69.40673	141,54953	141,54951	-0,00002
69.42003	141,56577	141,56573	-0,00004
69.82063	142,05461	142,05458	-0,00003
69.84047	142,07884	142,07881	-0,00003
70.21400	142,53548	142,53544	-0,00004
70.23115	142,55646	142,55642	-0,00004
70.24420	142,57243	142,57240	-0,00003
70.58611	142,99110	142,99200	0,00090
70.62476	143,03848	143,03844	-0,00004
70.63300	143,04857	143,04853	-0,00004
70.65918	143,08066	143,08063	-0,00003
70.68007	143,10626	143,10623	-0,00003
71.03493	143,54164	143,54160	-0,00004
71.05370	143,56468	143,56465	-0,00003
71.44140	144,04112	144,04111	-0,00001
71.45430	144,05699	144,05698	-0,00001
71.47306	144,08008	144,08005	-0,00003
71.48306	144,09282	144,09279	-0,00003
71.85212	144,54672	144,54673	0,00001
72.22502	145,00655	145,00655	0,0
72.27070	145,06293	145,06294	0,00001
72.30071	145,09996	145,09998	0,00002
72.66653	145,55191	145,55195	0,00004
73.07216	146,05386	146,05393	0,00007
73.08801	146,07350	146,07357	0,00007
73.10594	146,09570	146,09578	0,00008
73.11550	146,10754	146,10762	0,00008

73.46835	146.54497	146.54508	0.00011
73.48002	146.55946	146.55956	0.00010
73.80306	146.96051	146.96066	0.00015
73.85884	147.02983	147.02999	0.00016
73.86915	147.04263	147.04282	0.00019
73.88432	147.06149	147.06168	0.00019
73.89949	147.08034	147.08055	0.00021
73.92780	147.11552	147.11574	0.00022
74.27592	147.54858	147.54902	0.00044
74.28973	147.56577	147.56623	0.00046
74.64939	148.01389	148.01457	0.00068
74.66278	148.03058	148.03127	0.00069
74.67814	148.04973	148.05044	0.00071
74.69504	148.07080	148.07152	0.00072
74.70881	148.08798	148.08870	0.00072
74.73632	148.12228	148.12303	0.00075
75.08370	148.55591	148.55688	0.00097
75.09702	148.57254	148.57352	0.00098
75.40275	148.95471	148.95590	0.00119
75.45799	149.02382	149.02504	0.00122
75.48749	149.06073	149.06198	0.00125
75.50322	149.08041	149.08167	0.00126
75.51485	149.09496	149.09623	0.00127
75.54390	149.13133	149.13261	0.00128
75.87027	149.54008	149.54160	0.00152
75.88825	149.56262	149.56415	0.00153
76.22778	149.98848	149.99026	0.00178
76.25643	150.02444	150.02623	0.00179
76.27373	150.04617	150.04797	0.00180
76.28957	150.06607	150.06787	0.00180
76.31744	150.10104	150.10287	0.00183
76.34649	150.13754	150.13938	0.00184
76.67055	150.54477	150.54685	0.00208
77.02903	150.99593	150.99823	0.00230
77.05257	151.02556	151.02791	0.00235
77.07199	151.05003	151.05239	0.00236
77.09166	151.07481	151.07718	0.00237
77.11934	151.10968	151.11208	0.00240
77.14892	151.14694	151.14936	0.00242
77.46919	151.55078	151.55343	0.00265
77.86938	152.05614	152.05910	0.00296
77.88974	152.08188	152.08484	0.00296
77.94632	152.15341	152.15642	0.00301
78.26444	152.55586	152.55912	0.00326
78.66255	153.06026	153.06383	0.00357
78.74268	153.16190	153.16552	0.00362
79.04714	153.54834	153.55220	0.00386
79.06043	153.56523	153.56909	0.00386
79.43359	154.03957	154.04373	0.00416
79.45638	154.06856	154.07273	0.00417
79.53584	154.16968	154.17392	0.00424
79.82429	154.53700	154.54147	0.00447
79.83919	154.55598	154.56046	0.00448
79.85245	154.57289	154.57738	0.00449
80.18002	154.99060	154.99535	0.00475
80.22600	155.04930	155.05407	0.00477
80.24427	155.07262	155.07741	0.00479
80.25510	155.08644	155.09124	0.00480

80.32678	155.17795	155.18281	0.00486
80.61094	155.54100	155.54609	0.00509
80.62882	155.56386	155.56897	0.00511
81.00079	156.03978	156.04518	0.00540
81.01251	156.05478	156.06020	0.00542
81.03114	156.07864	156.08408	0.00544
81.04172	156.09218	156.09764	0.00546
81.39770	156.54840	156.55414	0.00574
81.41564	156.57141	156.57672	0.00531
81.78681	157.04785	157.05316	0.00531
81.79949	157.06413	157.06947	0.00534
81.81735	157.08710	157.09241	0.00531
81.82767	157.10034	157.10567	0.00533
81.84350	157.12068	157.12600	0.00532
82.56943	158.05482	158.06020	0.00538
82.58366	158.07315	158.07854	0.00539
82.60069	158.09511	158.10049	0.00538
82.61052	158.10777	158.11316	0.00539
82.95953	158.56797	158.56338	0.00541
83.34942	159.06163	159.06707	0.00544
83.36569	159.08267	159.08811	0.00544
83.39093	159.11531	159.12074	0.00543
83.72638	159.54938	159.55484	0.00546
83.73900	159.56572	159.57118	0.00546
84.11486	160.05281	160.05830	0.00549
84.12835	160.07030	160.07581	0.00551
84.14080	160.08644	160.09195	0.00551
84.16835	160.12218	160.12770	0.00552
84.50250	160.55594	160.56147	0.00553
84.51588	160.57332	160.57886	0.00554
84.87502	161.04021	161.04578	0.00557
84.88869	161.05798	161.06356	0.00558
84.90575	161.08018	161.08576	0.00558
84.91908	161.09753	161.10181	0.00428
84.94480	161.13100	161.13658	0.00558
85.25961	161.54092	161.54655	0.00563
85.27762	161.56439	161.57001	0.00562
85.28967	161.58009	161.58571	0.00562
85.60322	161.98897	161.99040	0.00143
85.64589	162.04465	162.05030	0.00565
85.66273	162.06662	162.07228	0.00566
85.68079	162.09019	162.09586	0.00567
85.69093	162.10342	162.10908	0.00566
85.71712	162.13760	162.14327	0.00567
86.03010	162.54643	162.55214	0.00571
86.37420	162.99651	163.00226	0.00575
86.40642	163.03870	163.04443	0.00573
86.42220	163.05936	163.06509	0.00573
86.45441	163.10152	163.10727	0.00575
86.45768	163.10580	163.11155	0.00575
86.48912	163.14697	163.15272	0.00575
86.79850	163.55235	163.55815	0.00580
87.18272	164.05652	164.06235	0.00583
87.20280	164.08289	164.08872	0.00583
87.25656	164.15350	164.15934	0.00584
87.56386	164.55740	164.56329	0.00589
87.95037	165.06615	165.07207	0.00592
87.99579	165.12598	165.13190	0.00592

88.02369	165.16275	165.16868	0.00593
88.31650	165.54878	165.55475	0.00597
88.33015	165.56679	165.57276	0.00597
88.71133	166.07005	166.07607	0.00602
88.78654	166.16945	166.17786	0.00841
89.07957	166.55696	166.56531	0.00835
89.09192	166.57332	166.58165	0.00833
89.40715	166.99072	166.99897	0.00825
89.43904	167.03297	167.04122	0.00825
89.47193	167.07657	167.08479	0.00822
89.54848	167.17804	167.18624	0.00820
89.82370	167.54311	167.55123	0.00812
89.83942	167.56396	167.57210	0.00814
89.85261	167.58148	167.58961	0.00813
90.19725	168.03925	168.04727	0.00802
90.21041	168.05675	168.06476	0.00801
90.23194	168.08536	168.09337	0.00801
90.30793	168.18640	168.19439	0.00799
90.58153	168.55043	168.55834	0.00791
90.59764	168.57187	168.57977	0.00790
90.91041	168.98853	168.99634	0.00781
90.95752	169.05133	169.05913	0.00780
90.96812	169.06546	169.07326	0.00780
90.99359	169.09943	169.10720	0.00777
91.06465	169.19418	169.20196	0.00778
91.33492	169.55486	169.56255	0.00769
91.64697	169.97177	169.97937	0.00760
91.71132	170.05782	170.06540	0.00758
91.72234	170.07254	170.08014	0.00760
91.73990	170.09602	170.10361	0.00759
91.74954	170.10893	170.11650	0.00757
92.08680	170.56029	170.56776	0.00747
92.46406	171.06589	171.07326	0.00737
92.47628	171.08229	171.08965	0.00736
92.49365	171.10559	171.11295	0.00736
92.50304	171.11818	171.12554	0.00736
92.51760	171.13771	171.14506	0.00735
92.83625	171.56544	171.57271	0.00727
93.13770	171.97060	171.97778	0.00718
93.19867	172.05260	172.05975	0.00715
93.21444	172.07382	172.08096	0.00714
93.22556	172.08878	172.09592	0.00714
93.24396	172.11354	172.12067	0.00713
93.25267	172.12524	172.13238	0.00714
93.58570	172.57361	172.58065	0.00704
93.93275	173.04146	173.04839	0.00693
93.94652	173.06003	173.06697	0.00694
93.96188	173.08076	173.08769	0.00693
93.97397	173.09708	173.10400	0.00692
94.00044	173.13278	173.13971	0.00693
94.32110	173.56575	173.57257	0.00682
94.33352	173.58255	173.58935	0.00680
94.63514	173.99031	173.99703	0.00672
94.67745	174.04755	174.05426	0.00671
94.69251	174.06793	174.07463	0.00670
94.70942	174.09082	174.09750	0.00668
94.72039	174.10565	174.11235	0.00670
94.74510	174.13908	174.14577	0.00669

95.37899	174.99805	175.00452	0.00647
95.42061	175.05452	175.06098	0.00646
95.43679	175.07648	175.08294	0.00646
95.46194	175.11060	175.11706	0.00646
95.48969	175.14827	175.15471	0.00644
95.78966	175.55565	175.56201	0.00636
96.16139	176.06116	176.06739	0.00623
96.19767	176.11053	176.11676	0.00623
96.19835	176.11147	176.11769	0.00622
96.23055	176.15529	176.16150	0.00621
96.52799	176.56042	176.56653	0.00611
96.89661	177.06314	177.06913	0.00599
96.91748	177.09163	177.09762	0.00599
96.97007	177.16342	177.16939	0.00597
97.26541	177.56685	177.57752	0.01067
97.63562	178.07320	178.08365	0.01045
97.65535	178.10019	178.11064	0.01045
97.70623	178.16985	178.18026	0.01041
98.30537	178.99109	179.00113	0.01004
98.36823	179.07736	179.08736	0.01000
98.44239	179.17917	179.18912	0.00995
99.08022	180.05600	180.06556	0.00956
99.10181	180.08572	180.09527	0.00955
99.17459	180.18591	180.19541	0.00950
99.81132	181.06372	181.07281	0.00909
99.82856	181.08751	181.09660	0.00909
99.83883	181.10168	181.11076	0.00908
99.90586	181.19423	181.20326	0.00903
100.48268	181.99159	182.00026	0.00867
100.53873	182.06918	182.07779	0.00861
100.55731	182.09489	182.10351	0.00862
100.56662	182.10779	182.11638	0.00859
100.63470	182.20204	182.21059	0.00855
101.21289	183.00354	183.01172	0.00818
101.26081	183.07007	183.07819	0.00812
101.26848	183.08070	183.08883	0.00813
101.29309	183.11485	183.12298	0.00813
101.36137	183.20966	183.21774	0.00808
101.95273	184.03174	184.03941	0.00767
101.96654	184.05095	184.05862	0.00767
101.98543	184.07726	184.08490	0.00764
102.01086	184.11264	184.12028	0.00764
102.01901	184.12398	184.13161	0.00763
102.68892	185.05774	185.06491	0.00717
102.70386	185.07860	185.08574	0.00714
102.71377	185.09242	185.09957	0.00715
102.74086	185.13025	185.13737	0.00712
102.75667	185.15231	185.15943	0.00712
103.35531	185.98897	185.99566	0.00669
103.39647	186.04655	186.04723	0.00068
103.41046	186.06615	186.06681	0.00066
103.42615	186.08810	186.08876	0.00066
103.43588	186.10172	186.10239	0.00067
104.07402	186.99596	186.99676	0.00080
104.11493	187.05336	187.05416	0.00080
104.12993	187.07440	187.07522	0.00082
104.14570	187.09653	187.09735	0.00082
104.15598	187.11096	187.11178	0.00082

104.18138	187.14661	187.14744	0.00083
104.83055	188.05891	188.05985	0.00094
104.86354	188.10533	188.10629	0.00096
105.54731	189.06879	189.06988	0.00109
105.56308	189.09105	189.09213	0.00108
105.57816	189.11232	189.11341	0.00109
105.58781	189.12593	189.12704	0.00111
105.61369	189.16246	189.16356	0.00110
106.25540	190.06915	190.07037	0.00122
106.27825	190.10149	190.10270	0.00121
106.32603	190.16908	190.17030	0.00122
106.96767	191.07811	191.07946	0.00135
106.98792	191.10683	191.10818	0.00135
107.03827	191.17827	191.17962	0.00135
107.67603	192.08421	192.08567	0.00146
107.74654	192.18451	192.18598	0.00147
108.31056	192.98773	192.98880	0.00107
108.38338	193.09155	193.09312	0.00157
108.45493	193.19359	193.19518	0.00159
109.01465	193.99280	193.99447	0.00167
109.06864	194.06998	194.07165	0.00167
109.08879	194.09879	194.10046	0.00167
109.16009	194.20074	194.20243	0.00169
109.72008	195.00244	195.00421	0.00177
109.77389	195.07957	195.08133	0.00176
109.78943	195.10184	195.10361	0.00177
109.79873	195.11516	195.11695	0.00179
109.86396	195.20869	195.21047	0.00178
110.47263	196.08244	196.08387	0.00143
110.49448	196.11385	196.11570	0.00185
110.50239	196.12521	196.12707	0.00186
110.56619	196.21692	196.21879	0.00187
111.13925	197.04166	197.04343	0.00177
111.15067	197.05809	197.05988	0.00179
111.17022	197.08626	197.08806	0.00180
111.26612	197.22447	197.22627	0.00180
111.83552	198.04604	198.04793	0.00189
111.84841	198.06467	198.06655	0.00188
111.86716	198.09174	198.09363	0.00189
112.53192	199.05321	199.05518	0.00197
112.54486	199.07195	199.07392	0.00197
112.56204	199.09685	199.09881	0.00196
112.59579	199.14572	199.14770	0.00198
112.61038	199.16685	199.16883	0.00198
113.17431	199.98457	199.98662	0.00205
113.22717	200.06129	200.06337	0.00208
113.24142	200.08200	200.08405	0.00205
113.25784	200.10583	200.10789	0.00206
113.86780	200.99248	200.99503	0.00255
113.98360	201.16103	201.16316	0.00213
114.61030	202.07446	202.07666	0.00220
114.64252	202.12148	202.12369	0.00221
115.29723	203.07809	203.08035	0.00226
115.33794	203.13765	203.13992	0.00227
115.36487	203.17705	203.17932	0.00227
115.98283	204.08228	204.08460	0.00232
116.05181	204.18346	204.18579	0.00233
116.59824	204.98581	204.98818	0.00237

116.65267	205.06581	205.06819	0.00238
116.66947	205.09052	205.09289	0.00237
116.73850	205.19200	205.19439	0.00239
117.32943	206.06194	206.06436	0.00242
117.34715	206.08806	206.09048	0.00242
117.36027	206.10730	206.10981	0.00242
117.42212	206.19856	206.20098	0.00242
118.01898	207.07941	207.08186	0.00245
118.03723	207.10637	207.10882	0.00245
118.10567	207.20750	207.20995	0.00245
118.66207	208.03059	208.03308	0.00249
118.69606	208.08093	208.08342	0.00249
118.71686	208.11174	208.11423	0.00249
118.78600	208.21416	208.21665	0.00249
119.37405	209.08626	209.08896	0.00270
119.39809	209.12196	209.12466	0.00270
119.46577	209.22246	209.22517	0.00271
120.03108	210.06287	210.06559	0.00272
120.04955	210.09035	210.09307	0.00272
120.07650	210.13045	210.13318	0.00273
120.14422	210.23125	210.23399	0.00274
120.69570	211.05307	211.05582	0.00275
120.70875	211.07254	211.07529	0.00275
120.72532	211.09726	211.10002	0.00276
120.75634	211.14354	211.14629	0.00275
120.82023	211.23888	211.24163	0.00275
121.31960	211.98477	211.98720	0.00243
121.36324	212.05002	212.05279	0.00277
121.37423	212.06644	212.06922	0.00278
121.38385	212.08084	212.08360	0.00276
121.39921	212.10381	212.10657	0.00276
121.99245	212.99190	212.99466	0.00276
122.04398	213.06912	213.07191	0.00279
122.07317	213.11288	213.11565	0.00277
122.10508	213.16071	213.16349	0.00278
122.11932	213.18207	213.18484	0.00277
122.70662	214.06352	214.06629	0.00277
122.72301	214.08813	214.09092	0.00279
122.74347	214.11888	214.12165	0.00277
123.38241	215.08005	215.08282	0.00277
123.44631	215.17628	215.17907	0.00279
124.04842	216.08426	216.08702	0.00276
124.64548	216.98651	216.98901	0.00250
124.71354	217.08949	217.09199	0.00250
124.75644	217.15440	217.15691	0.00251
124.78158	217.19244	217.19496	0.00252
125.36145	218.07098	218.07347	0.00249
125.38010	218.09926	218.10176	0.00250
125.42318	218.16461	218.16710	0.00249
125.44706	218.20084	218.20333	0.00249
125.96289	218.98409	218.98657	0.00248
126.02045	219.07158	219.07405	0.00247
126.04224	219.10469	219.10718	0.00249
126.11074	219.20885	219.21133	0.00248
126.62175	219.98659	219.98904	0.00245
126.68067	220.07634	220.07880	0.00246
126.70543	220.11406	220.11654	0.00248
126.77217	220.21577	220.21824	0.00247

127.34390	221.08804	221.09047	0.00243
127.36623	221.12215	221.12457	0.00242
127.43299	221.22412	221.22655	0.00243
127.97050	222.04601	222.04841	0.00240
127.98264	222.06461	222.06699	0.00238
128.00076	222.09233	222.09472	0.00239
128.01999	222.12177	222.12416	0.00239
128.09189	222.23184	222.23424	0.00240
128.62709	223.05209	223.05445	0.00236
128.63934	223.07088	223.07324	0.00236
128.65622	223.09679	223.09915	0.00236
128.68484	223.14069	223.14305	0.00236
128.74883	223.23888	223.24125	0.00237
129.23466	223.98512	223.98720	0.00208
129.28354	224.06026	224.06258	0.00232
129.30934	224.09993	224.10225	0.00232
129.34625	224.15669	224.15900	0.00231
129.40518	224.24733	224.24963	0.00230
129.88900	224.99216	224.99442	0.00226
129.93940	225.06982	225.07208	0.00226
129.95375	225.09195	225.09420	0.00225
129.96721	225.11267	225.11494	0.00227
130.05965	225.25517	225.25742	0.00225
130.59126	226.07550	226.07770	0.00220
130.60619	226.09856	226.10076	0.00220
130.61747	226.11600	226.11818	0.00218
131.24182	227.08145	227.08357	0.00212
131.27361	227.13066	227.13278	0.00212
131.89096	228.08745	228.08950	0.00205
131.96682	228.20515	228.20719	0.00204
132.46949	228.98592	228.98792	0.00200
132.53513	229.08797	229.08995	0.00198
132.60224	229.19234	229.19432	0.00198
133.16610	230.07013	230.07208	0.00195
133.18519	230.09990	230.10182	0.00192
133.75152	230.98331	230.98560	0.00229
133.81161	231.07715	231.07901	0.00186
133.82918	231.10458	231.10645	0.00187
133.89535	231.20795	231.20980	0.00185
134.39303	231.98608	231.98788	0.00180
134.46139	232.09306	232.09485	0.00179
134.53872	232.21411	232.21590	0.00179
135.03913	232.99825	232.99995	0.00170
135.09365	233.08376	233.08546	0.00170
135.11572	233.11836	233.12008	0.00172
135.18290	233.22377	233.22547	0.00170
135.70575	234.04489	234.04651	0.00162
135.73114	234.08481	234.08643	0.00162
135.75352	234.11998	234.12161	0.00163
135.82365	234.23026	234.23185	0.00159
136.34691	235.05380	235.05534	0.00154
136.37401	235.09651	235.09803	0.00152
136.39993	235.13733	235.13887	0.00154
136.46465	235.23932	235.24083	0.00151
136.93722	235.98465	235.98610	0.00145
136.98405	236.05858	236.06001	0.00143
136.99766	236.08006	236.08149	0.00143
137.01171	236.10225	236.10368	0.00143



137.03398	236.13741	236.13883	0.00142
137.10347	236.24715	236.24855	0.00140
137.57472	236.99200	236.99334	0.00134
137.62366	237.06943	237.07076	0.00133
137.65075	237.11230	237.11361	0.00131
137.67903	237.15704	237.15835	0.00131
137.74062	237.25452	237.25581	0.00129
138.25436	238.06834	238.06954	0.00120
138.28196	238.11211	238.11337	0.00126
138.37747	238.26358	238.26482	0.00124
138.89548	239.08594	239.08712	0.00118
138.92299	239.12965	239.13081	0.00116
138.95280	239.17703	239.17819	0.00116
139.01182	239.27083	239.27197	0.00114
139.52132	240.08141	240.08247	0.00106
139.54167	240.11380	240.11487	0.00107
139.55667	240.13770	240.13875	0.00105
140.08996	240.98770	240.98866	0.00096
140.15594	241.09297	241.09393	0.00096
140.23221	241.21469	241.21564	0.00095
140.78169	242.09250	242.09335	0.00085
141.39692	243.07730	243.07800	0.00070
141.41734	243.11002	243.11073	0.00071
141.96503	243.98845	243.98904	0.00059
142.02610	244.08650	244.08707	0.00057
142.04591	244.11832	244.11888	0.00056
142.59388	244.99902	244.99948	0.00046
142.64981	245.08902	245.08946	0.00044
142.67049	245.12230	245.12273	0.00043
142.73454	245.22537	245.22578	0.00041
143.28212	246.10748	246.10777	0.00029
143.88262	247.07669	247.07685	0.00016
143.90163	247.10739	247.10709	-0.00030
143.92008	247.13722	247.13689	-0.00033
143.98457	247.24142	247.24110	-0.00032
144.44560	247.98709	247.98670	-0.00039
144.49321	248.06415	248.06375	-0.00040
144.51627	248.10149	248.10107	-0.00042
144.60687	248.24820	248.24777	-0.00043
145.11851	249.07750	249.07697	-0.00053
145.14456	249.11975	249.11923	-0.00052
145.16485	249.15268	249.15214	-0.00054
145.22947	249.25752	249.25699	-0.00053
145.73186	250.07350	250.07285	-0.00065
145.76021	250.11958	250.11894	-0.00064
145.84921	250.26428	250.26363	-0.00065
146.29667	250.99245	250.99183	-0.00062
146.35291	251.08403	251.08328	-0.00075
146.38302	251.13309	251.13232	-0.00077
146.96853	252.08780	252.08692	-0.00088
146.99365	252.12880	252.12791	-0.00089
147.08730	252.28169	252.28077	-0.00092
147.58702	253.09827	253.09725	-0.00102
147.61781	253.14864	253.14760	-0.00104
147.70325	253.28839	253.28735	-0.00104
148.19632	254.09573	254.09459	-0.00114
148.21316	254.12334	254.12218	-0.00116
148.73942	254.98651	254.98521	-0.00130

148.80863	255.10013	255.09883	-0.00130
148.87623	255.21115	255.20982	-0.00133
149.40383	256.07837	256.07693	-0.00144
149.42613	256.11499	256.11362	-0.00137
149.50282	256.24121	256.23980	-0.00141
150.01615	257.08667	257.08514	-0.00153
150.03758	257.12207	257.12046	-0.00161
150.10107	257.22656	257.22512	-0.00144
150.11360	257.24731	257.24578	-0.00153
150.62900	258.09790	258.09623	-0.00167
150.65089	258.13403	258.13238	-0.00165
151.21198	259.06177	259.05990	-0.00187
151.23726	259.10352	259.10177	-0.00175
151.25930	259.14014	259.13824	-0.00190
151.32248	259.24463	259.24281	-0.00182
151.84089	260.10352	260.10154	-0.00198
151.86380	260.14160	260.13953	-0.00207
151.92984	260.25098	260.24904	-0.00194
152.42599	261.07471	261.07251	-0.00220
152.45175	261.11743	261.11529	-0.00214
152.47438	261.15503	261.15288	-0.00215
152.53765	261.26025	261.25801	-0.00224
152.97430	261.98633	261.98405	-0.00228
153.02075	262.06372	262.06135	-0.00237
153.04596	262.10571	262.10331	-0.00240
153.14307	262.26733	262.26495	-0.00238
153.57939	262.99438	262.99183	-0.00255
153.63807	263.09229	263.08970	-0.00259
153.66439	263.13623	263.13361	-0.00262
153.74791	263.27563	263.27290	-0.00273
154.23385	264.08691	264.08412	-0.00279
154.26135	264.13281	264.13005	-0.00276
154.33030	264.24805	264.24527	-0.00278
154.35157	264.28369	264.28082	-0.00287
154.83993	265.10059	265.09764	-0.00295
154.86963	265.15039	265.14736	-0.00303
155.42393	266.07935	266.07612	-0.00323
155.44067	266.10742	266.10353	-0.00389
155.45688	266.13477	266.13074	-0.00403
155.55537	266.29980	266.29598	-0.00382
155.96632	266.98999	266.98599	-0.00400
156.03801	267.11035	267.10646	-0.00389
156.07174	267.16724	267.16315	-0.00409
156.15588	267.30859	267.30460	-0.00399
156.63327	268.11182	268.10779	-0.00403
157.15322	268.98804	268.98399	-0.00405
157.21331	269.08936	269.08535	-0.00401
157.23545	269.12671	269.12268	-0.00403
157.74630	269.98926	269.98519	-0.00407
157.79448	270.07080	270.06659	-0.00421
157.80961	270.09644	270.09217	-0.00427
157.83134	270.13306	270.12889	-0.00417
158.38700	271.07324	271.06886	-0.00438
158.40615	271.10547	271.10130	-0.00417
158.42823	271.14307	271.13869	-0.00438
158.97632	272.07202	272.06758	-0.00444
159.00016	272.11255	272.10802	-0.00453
159.02375	272.15234	272.14805	-0.00429

159.55936	273.06201	273.05750	-0.00451
159.57088	273.08154	273.07708	-0.00446
159.59435	273.12134	273.11696	-0.00438
159.61639	273.15894	273.15441	-0.00453
159.67724	273.26245	273.25786	-0.00459
160.10444	273.98926	273.98400	-0.00526
160.15961	274.08301	274.07852	-0.00449
160.18216	274.12158	274.11691	-0.00467
160.20243	274.15601	274.15143	-0.00458
160.69554	274.99658	274.99175	-0.00483
160.74178	275.07544	275.07061	-0.00483
160.75552	275.09888	275.09405	-0.00483
160.77825	275.13745	275.13282	-0.00463
160.79884	275.17261	275.16795	-0.00466
160.86068	275.27832	275.27345	-0.00487
161.33688	276.09155	276.08662	-0.00493
161.36345	276.13696	276.13203	-0.00493
161.45088	276.28638	276.28148	-0.00490
161.92374	277.09546	277.09042	-0.00504
161.94155	277.12598	277.12092	-0.00506
161.95777	277.15356	277.14869	-0.00487
162.04006	277.29468	277.28960	-0.00508
162.51340	278.10596	278.10085	-0.00511
162.54348	278.15747	278.15112	-0.00635
162.62760	278.30200	278.29550	-0.00650
163.02901	278.99121	278.98492	-0.00629
163.08812	279.09277	279.08651	-0.00626
163.11475	279.13843	279.13228	-0.00615
163.13200	279.16821	279.16193	-0.00628
163.66475	280.08447	280.07858	-0.00589
163.68451	280.11865	280.11261	-0.00604
163.70197	280.14868	280.14266	-0.00602
163.71219	280.16626	280.16026	-0.00600
163.80084	280.31885	280.31296	-0.00589
164.19017	280.98999	280.98239	-0.00760
164.24851	281.09058	281.08470	-0.00588
164.27002	281.12769	281.12180	-0.00589
164.77049	281.99146	281.98590	-0.00556
164.83508	282.10303	282.09752	-0.00551
164.85718	282.14136	282.13570	-0.00566
165.35600	283.00391	282.99851	-0.00540
165.39886	283.07813	283.07271	-0.00542
165.41544	283.10669	283.10141	-0.00528
165.43734	283.14478	283.13932	-0.00546
165.99022	284.10254	284.09742	-0.00512
166.01684	284.14868	284.14360	-0.00508
166.09130	284.27783	284.27276	-0.00507
166.55619	285.08472	285.07990	-0.00482
166.57773	285.12231	285.11732	-0.00499
166.59925	285.15967	285.15473	-0.00494
166.67007	285.28271	285.27779	-0.00492
167.07751	285.99121	285.98639	-0.00482
167.12604	286.07568	286.07084	-0.00484
167.15589	286.12744	286.12280	-0.00464
167.17616	286.16284	286.15808	-0.00476
167.70905	287.09106	287.08648	-0.00458
167.73739	287.14038	287.13590	-0.00448
167.75650	287.17383	287.16922	-0.00461

167.81688	287.27905	287.27452	-0.00453
168.27945	288.08618	288.08189	-0.00429
168.30706	288.13452	288.13012	-0.00440
168.32702	288.16943	288.16499	-0.00444
168.86349	289.10718	289.10293	-0.00425
168.89102	289.15527	289.15110	-0.00417
168.97098	289.29517	289.29104	-0.00413
169.44485	290.12500	290.12109	-0.00391
169.54607	290.30249	290.29854	-0.00395
169.93872	290.99121	290.98742	-0.00379
170.00602	291.10938	291.10558	-0.00380
170.02436	291.14160	291.13779	-0.00381
170.03984	291.16870	291.16497	-0.00373
170.12091	291.31128	291.30735	-0.00393
170.57781	292.11401	292.11046	-0.00355
170.60473	292.16138	292.15781	-0.00357
170.69323	292.31714	292.31351	-0.00363
171.07486	292.98901	292.98239	-0.00662
171.13174	293.08911	293.08561	-0.00350
171.15075	293.12256	293.11909	-0.00347
171.16756	293.15234	293.14873	-0.00361
171.18483	293.18262	293.17915	-0.00347
171.64331	293.99097	293.98764	-0.00333
171.69175	294.07642	294.07314	-0.00328
171.72277	294.13135	294.12789	-0.00346
171.83680	294.33252	294.32919	-0.00333
172.25713	295.07495	295.07182	-0.00313
172.27423	295.10522	295.10205	-0.00317
172.29494	295.14185	295.13866	-0.00319
172.40731	295.34058	295.33740	-0.00318
172.82735	296.08398	296.08081	-0.00317
172.84440	296.11401	296.11100	-0.00301
172.86204	296.14526	296.14223	-0.00303
173.38100	297.06519	297.06211	-0.00308
173.39952	297.09790	297.09497	-0.00293
173.41449	297.12451	297.12153	-0.00298
173.43338	297.15796	297.15504	-0.00292
173.90097	297.98804	297.98524	-0.00280
173.97311	298.11621	298.11343	-0.00278
173.99795	298.16040	298.15757	-0.00283
174.51315	299.07066	299.07391	-0.00275
174.52521	299.09814	299.09538	-0.00276
174.54576	299.13477	299.13195	-0.00282
174.56704	299.17261	299.16983	-0.00278
175.08179	300.08960	300.08695	-0.00265
175.10891	300.13794	300.13532	-0.00262
175.12761	300.17139	300.16867	-0.00272
175.58692	300.99072	300.98830	-0.00242
175.64254	301.09009	301.08764	-0.00245
175.65699	301.11597	301.11345	-0.00252
175.67605	301.14990	301.14748	-0.00242
175.69632	301.18628	301.18370	-0.00258
175.75484	301.29077	301.28823	-0.00254
176.20690	302.09888	302.09645	-0.00243
176.23348	302.14648	302.14400	-0.00248
176.77392	303.11401	303.11173	-0.00228
176.80212	303.16455	303.16227	-0.00228
176.81183	303.18188	303.17969	-0.00219

176.88075	303.30542	303.30323	-0.00219
177.31559	304.08545	304.08324	-0.00221
177.33438	304.11914	304.11697	-0.00217
177.35763	304.16089	304.15871	-0.00218
177.44172	304.31201	304.30969	-0.00232

180.88000

262.09183

306.17900

170.00000

0.11842-01

0.10675-01

0.35X

0.11842-01

0.10675-01

0.35X

0.11842-01

0.10675-01

0.35X

0.11842-01

0.10675-01

0.35X

TABLE 2.4 - FINAL DATA OUTPUT FOR SPECTRUM H

<u>reference distances</u>	<u>reference masses</u>		
16.24020	84.96565		
93.91535	180.98880		
144.57701	262.99183		
198.33906	366.97920		
227.55528	430.97280		
5			
0.1263E-04	0.1964E-04	0.1867E-04	0.3537E-04
0.1281E-04	0.1981E-04	0.1922E-04	0.3593E-04
0.1018E 01	0.3522E 01	0.4838E 01	0.1253E 02
0.2253E 01	0.5140E 01	0.6770E 01	0.1472E 02

distance	mass $M_1$	mass $M_2$	$M_2 - M_1$
16.30294	85.02876	85.03153	0.00277
16.33900	85.06506	85.06778	0.00272
16.37531	85.10164	85.10429	0.00265
17.30181	86.03741	86.03852	0.00111
17.33786	86.07393	86.07497	0.00104
18.27472	87.02551	87.02508	-0.00043
18.29416	87.04530	87.04485	-0.00045
19.26212	88.03401	88.03215	-0.00186
20.24389	89.04248	89.03929	-0.00319
21.22017	90.05092	90.04653	-0.00439
22.19119	91.05949	91.05401	-0.00548
23.15615	92.06729	92.06082	-0.00647
24.04560	93.00108	92.99520	-0.00588
24.08240	93.03983	93.03250	-0.00733
24.11688	93.07613	93.06877	-0.00736
24.55104	93.53381	93.52608	-0.00773
25.03615	94.04651	94.03840	-0.00811
25.07232	94.08479	94.07666	-0.00813
25.50369	94.54198	94.53351	-0.00847
25.95193	95.01817	95.00942	-0.00875
26.02243	95.09319	95.08438	-0.00881
26.44563	95.54405	95.53497	-0.00908
26.96672	96.10066	96.09128	-0.00938
27.90677	97.10884	97.09899	-0.00985
28.80838	98.08070	98.07048	-0.01022
28.84082	98.11575	98.10809	-0.00766
29.68561	99.03088	99.02246	-0.00842
29.77213	99.12485	99.11635	-0.00850
30.57737	100.00146	99.99232	-0.00914
30.61222	100.03947	100.03032	-0.00915
30.66393	100.09592	100.08671	-0.00921
31.49900	101.00948	101.00143	-0.00805
31.53331	101.04710	101.03728	-0.00982
31.98929	101.54776	101.53765	-0.01011
32.44835	102.05305	102.04267	-0.01038
33.35120	103.05046	103.03959	-0.01087
33.36269	103.06319	103.05231	-0.01088
34.23771	104.03450	104.02323	-0.01127
34.27033	104.07079	104.05952	-0.01127
35.14101	105.04195	105.03036	-0.01159
35.17416	105.07899	105.06742	-0.01157
35.58306	105.53671	105.52500	-0.01171
36.03477	106.04349	106.03168	-0.01181
36.07224	106.08559	106.07376	-0.01183
36.47976	106.54391	106.53201	-0.01190
36.93468	107.05672	107.04473	-0.01197
36.96797	107.09428	107.08230	-0.01198
37.37010	107.54865	107.53663	-0.01202
37.82491	108.06372	108.05167	-0.01205
37.85801	108.10124	108.09143	-0.00981
38.25635	108.55345	108.54343	-0.01002
38.74502	109.10947	109.09923	-0.01024
39.56368	110.04411	110.03357	-0.01054
39.62724	110.11684	110.10627	-0.01057
40.42565	111.03249	111.02168	-0.01081
40.50631	111.12521	111.11438	-0.01083
41.26715	112.00163	111.99360	-0.00803
41.30049	112.04012	112.02913	-0.01099

41.38031	112.13228	112.12127	-0.01101
42.13836	113.00941	112.99828	-0.01113
42.17011	113.04622	113.03510	-0.01112
42.17432	113.05110	113.03998	-0.01112
42.25160	113.14073	113.12959	-0.01114
42.60229	113.54790	113.53673	-0.01117
43.03496	114.05124	114.04006	-0.01118
43.90029	115.06125	115.05007	-0.01118
44.75827	116.06705	116.05596	-0.01109
45.55259	117.00211	116.99449	-0.00762
45.61322	117.07364	117.06598	-0.00766
45.61751	117.07869	117.07104	-0.00765
46.00373	117.53484	117.52703	-0.00781
46.43321	118.04311	118.03515	-0.00796
46.46785	118.08415	118.07618	-0.00797
46.85413	118.54231	118.53421	-0.00810
47.23875	118.99939	118.99117	-0.00822
47.27682	119.04468	119.03644	-0.00824
47.31740	119.09296	119.08472	-0.00824
47.69990	119.54857	119.54022	-0.00835
48.07992	120.00206	119.99362	-0.00844
48.12052	120.05057	120.04212	-0.00845
48.13192	120.06419	120.05574	-0.00845
48.16019	120.09798	120.08950	-0.00848
48.53932	120.55145	120.54290	-0.00855
48.94307	121.03529	121.02669	-0.00860
48.95803	121.05324	121.04464	-0.00860
48.97365	121.07198	121.06338	-0.00860
49.00347	121.10776	121.09915	-0.00861
49.78109	122.04266	122.03397	-0.00869
49.80012	122.06558	122.05688	-0.00870
49.81135	122.07912	122.07042	-0.00870
49.84162	122.11559	122.10689	-0.00870
50.61575	123.05013	123.04138	-0.00875
50.63505	123.07347	123.06472	-0.00875
50.67616	123.12320	123.11446	-0.00874
51.39925	123.99960	123.99360	-0.00600
51.43077	124.03789	124.02914	-0.00875
51.44684	124.05739	124.04865	-0.00874
51.50668	124.13007	124.12134	-0.00873
52.25879	125.04539	125.03674	-0.00865
52.33528	125.13869	125.13001	-0.00868
52.66909	125.54616	125.53755	-0.00861
53.08123	126.05016	126.04161	-0.00855
53.08772	126.05811	126.04956	-0.00855
53.15929	126.14574	126.13720	-0.00854
53.49038	126.55150	126.54304	-0.00846
53.90134	127.05608	127.04769	-0.00839
53.90814	127.06442	127.05906	-0.00536
53.98077	127.15370	127.14832	-0.00538
54.30866	127.55714	127.55167	-0.00547
54.72047	128.06474	128.05917	-0.00557
55.53179	129.06773	129.06197	-0.00576
55.55573	129.09738	129.09161	-0.00577
56.33912	130.06967	130.06377	-0.00590
56.35029	130.08356	130.07766	-0.00590
56.71759	130.54070	130.53474	-0.00596
57.08183	130.99480	130.98883	-0.00597



57.09159	131.00699	131.00101	-0.00598
57.12735	131.05161	131.04563	-0.00598
57.15865	131.09068	131.08471	-0.00597
57.52448	131.54774	131.54174	-0.00600
57.88570	131.99982	131.99536	-0.00446
57.96366	132.09750	132.09148	-0.00602
58.32470	132.55029	132.54427	-0.00602
58.69153	133.01114	133.00513	-0.00601
58.71650	133.04253	133.03652	-0.00601
58.72586	133.05431	133.04830	-0.00601
58.73790	133.06944	133.06344	-0.00600
58.76614	133.10497	133.09895	-0.00602
59.12512	133.55687	133.55089	-0.00598
59.52302	134.05869	134.05273	-0.00596
59.53776	134.07730	134.07134	-0.00596
59.56585	134.11275	134.10680	-0.00595
60.30561	135.04839	135.04252	-0.00587
60.33434	135.08478	135.07893	-0.00585
60.36198	135.11980	135.11396	-0.00584
61.12756	136.09177	136.08606	-0.00571
61.15587	136.12778	136.12207	-0.00571
61.87415	137.04295	137.03741	-0.00554
61.88957	137.06264	137.05711	-0.00553
61.94690	137.13582	137.13030	-0.00552
62.66109	138.04915	138.04383	-0.00532
62.73427	138.14291	138.13911	-0.00380
63.05170	138.54994	138.54611	-0.00383
63.44514	139.05530	139.05138	-0.00392
63.51951	139.15092	139.14701	-0.00391
63.83265	139.55392	139.54996	-0.00396
64.22339	140.05762	140.05362	-0.00400
64.30166	140.15862	140.15461	-0.00401
64.61323	140.56104	140.55701	-0.00403
65.00685	141.07027	141.06622	-0.00405
65.01471	141.08043	141.07639	-0.00404
65.08046	141.16559	141.16154	-0.00405
65.78273	142.07671	142.07266	-0.00405
65.79138	142.08795	142.08389	-0.00406
66.48725	142.99370	142.99200	-0.00170
66.55689	143.08450	143.08047	-0.00403
66.91010	143.54547	143.54147	-0.00400
67.25883	144.00133	143.99736	-0.00397
67.30299	144.05913	144.05514	-0.00399
67.67677	144.54863	144.54470	-0.00393
68.02802	145.00938	145.00551	-0.00387
68.06016	145.05157	145.04771	-0.00386
68.07242	145.06767	145.06381	-0.00386
68.09998	145.10388	145.10001	-0.00387
68.44303	145.55473	145.55092	-0.00381
68.82440	146.05678	146.05303	-0.00375
68.83638	146.07256	146.06882	-0.00374
69.20682	146.56107	146.55740	-0.00367
69.56816	147.03836	147.03478	-0.00358
69.59025	147.06757	147.06504	-0.00253
69.60192	147.08299	147.08048	-0.00251
69.62864	147.11832	147.11582	-0.00250
70.30757	148.01746	148.01538	-0.00208
71.02477	148.97026	148.96863	-0.00163

71.06546	149.02440	149.02281	-0.00159
71.09559	149.06451	149.06292	-0.00159
71.12015	149.09720	149.09563	-0.00157
71.14752	149.13364	149.13210	-0.00154
71.79029	149.99063	149.98952	-0.00111
71.81585	150.02475	150.02367	-0.00108
71.83180	150.04605	150.04498	-0.00107
72.54416	150.99886	150.99831	-0.00055
72.56688	151.02930	151.02878	-0.00052
72.58515	151.05379	151.05326	-0.00053
72.65604	151.14879	151.14832	-0.00047
72.95740	151.55298	151.55275	-0.00023
73.33564	152.06104	152.06112	0.00008
73.40625	152.15599	152.15612	0.00013
73.70686	152.56050	152.56089	0.00039
74.08260	153.06689	153.06758	0.00069
74.15469	153.16415	153.16491	0.00076
74.82776	154.07364	154.07498	0.00134
74.89987	154.17123	154.17263	0.00140
75.50505	154.99153	154.99350	0.00197
75.57408	155.08524	155.08727	0.00203
75.64302	155.17885	155.18095	0.00210
76.31454	156.09219	156.09494	0.00275
77.02654	157.06349	157.06696	0.00347
77.05250	157.09898	157.10214	0.00316
77.38507	157.55376	157.55690	0.00314
77.76306	158.07144	158.07457	0.00313
78.48713	159.06551	159.06861	0.00310
78.49965	159.08272	159.08583	0.00311
78.52467	159.11713	159.12024	0.00311
79.22791	160.08572	160.08885	0.00313
80.60407	161.98969	161.99040	0.00071
80.64540	162.04704	162.05028	0.00324
81.32896	162.99713	163.00045	0.00332
81.36842	163.05206	163.05538	0.00332
81.37245	163.05766	163.06100	0.00334
81.43723	163.14787	163.15121	0.00334
82.09105	164.05965	164.06309	0.00344
82.81285	165.06918	165.07277	0.00359
82.87987	165.16307	165.16668	0.00361
83.53028	166.07568	166.07943	0.00375
84.21110	167.03365	167.04127	0.00762
84.24480	167.08115	167.08873	0.00758
84.31442	167.17928	167.18682	0.00754
84.93705	168.05817	168.06531	0.00714
85.59467	168.98897	168.99570	0.00673
85.67365	169.10092	169.10761	0.00669
86.28725	169.97203	169.97834	0.00631
86.30153	169.99232	169.99216	-0.00016
87.68835	171.96953	171.97506	0.00553
89.09832	173.99149	173.99630	0.00481
89.83725	175.05588	175.06035	0.00447
90.53373	176.06212	176.06625	0.00413
91.22625	177.06549	177.06934	0.00385
91.29403	177.16385	177.16767	0.00382
91.92199	178.07642	178.08552	0.00910
92.61286	179.08311	179.09155	0.00844
92.67878	179.17932	179.18770	0.00838

93.27939	180.05705	180.06487	0.00782
93.30005	180.08730	180.09507	0.00777
93.96592	181.06297	181.07017	0.00720
94.59819	181.99190	181.99851	0.00661
95.28584	183.00490	183.01089	0.00599
97.30155	185.99055	185.99482	0.00427
98.01725	187.05647	187.05601	-0.00046
99.36426	189.07092	189.07040	-0.00052
99.42665	189.16451	189.16397	-0.00054
100.03045	190.07124	190.07069	-0.00055
100.70311	191.08395	191.08339	-0.00056
100.76705	191.18034	191.17980	-0.00054
101.37111	192.09232	192.09177	-0.00055
101.96375	192.98915	192.98880	-0.00035
102.03616	193.09886	193.09835	-0.00051
102.10029	193.19606	193.19556	-0.00050
102.69539	194.09923	194.09877	-0.00046
103.34185	195.08273	195.08232	-0.00041
103.99775	196.08316	196.08280	-0.00036
105.31116	198.09419	198.09400	-0.00019
106.59085	200.06352	200.06357	0.00005
107.19387	200.99492	200.99503	0.00011
107.24130	201.06825	201.06837	0.00012
107.89226	202.07632	202.07651	0.00019
108.53861	203.07974	203.08003	0.00029
109.18283	204.08237	204.08274	0.00037
109.76291	204.98727	204.98774	0.00047
109.82588	205.08563	205.08511	0.00048
110.46850	206.09070	206.09130	0.00060
112.37501	209.08707	209.08807	0.00100
113.01255	210.09390	210.09505	0.00115
113.63031	211.07184	211.07305	0.00121
113.64671	211.09784	211.09905	0.00121
114.20593	211.98512	211.98720	0.00208
114.83903	212.99188	212.99328	0.00140
114.88740	213.06889	213.07031	0.00142
115.51276	214.06590	214.06741	0.00151
116.14929	215.08311	215.08474	0.00163
116.77470	216.08492	216.08667	0.00175
117.33621	216.98637	216.98910	0.00273
117.39955	217.08818	217.09091	0.00273
118.02271	218.09105	218.09375	0.00270
118.57590	218.98326	218.98594	0.00268
118.64860	219.10065	219.10335	0.00270
121.11053	223.09454	223.09723	0.00269
121.65533	223.98346	223.98720	0.00374
121.70289	224.06113	224.06384	0.00271
121.72484	224.09698	224.09970	0.00272
122.27215	224.99185	224.99458	0.00273
122.33773	225.09920	225.10192	0.00272
122.93354	226.07564	226.07839	0.00275
123.54150	227.07420	227.07697	0.00277
124.15589	228.08557	228.08838	0.00281
124.76643	229.09285	229.09624	0.00339
125.37322	230.09615	230.09944	0.00329
125.90808	230.98236	230.98560	0.00324
125.97826	231.09877	231.10196	0.00319
126.51237	231.98566	231.98880	0.00314

126.57497	232.08972	232.09285	0.00313
127.12048	232.99753	233.00058	0.00305
127.17113	233.08189	233.08495	0.00306
127.18939	233.11232	233.11536	0.00304
127.77099	234.08240	234.08537	0.00297
128.37792	235.09688	235.09978	0.00290
128.90724	235.98344	235.98627	0.00283
128.97912	236.10397	236.10680	0.00283
129.55350	237.06816	237.07092	0.00276
129.57865	237.11043	237.11317	0.00274
130.14883	238.06961	238.07229	0.00268
130.75086	239.08449	239.08728	0.00279
131.34079	240.08109	240.08376	0.00267
131.93569	241.08820	241.09075	0.00255
132.52866	242.09415	242.09660	0.00245
133.05125	242.98247	242.98560	0.00313
133.12141	243.10185	243.10419	0.00234
133.71256	244.10893	244.11115	0.00222
134.30076	245.11307	245.11518	0.00211
134.87755	246.09975	246.10176	0.00201
135.46018	247.09846	247.10035	0.00189
136.04225	248.09824	248.10069	0.00245
136.61136	249.07773	249.07995	0.00222
136.63089	249.11137	249.11360	0.00223
137.19133	250.07790	250.07992	0.00202
137.21096	250.11179	250.11380	0.00201
137.71926	250.99011	250.99183	0.00172
137.76844	251.07516	251.07694	0.00178
137.79941	251.12874	251.13051	0.00177
138.35605	252.09262	252.09418	0.00156
138.93188	253.09171	253.09304	0.00133
139.50985	254.09651	254.09760	0.00109
140.01971	254.98457	254.98546	0.00089
140.08665	255.10129	255.10214	0.00085
140.66313	256.10742	256.10812	0.00070
141.24152	257.11890	257.11945	0.00055
141.79895	258.09570	258.09603	0.00033
141.81509	258.12402	258.12434	0.00032
142.37148	259.10107	259.10102	-0.00005
142.39009	259.13354	259.13372	0.00018
142.94539	260.11133	260.11128	-0.00005
143.51447	261.11353	261.11324	-0.00029
144.07644	262.10620	262.10548	-0.00072
144.63514	263.09473	263.09413	-0.00060
144.65529	263.13013	263.12983	-0.00030
145.19451	264.08618	264.08557	-0.00061
145.21484	264.12231	264.12164	-0.00067
145.76314	265.09619	265.09534	-0.00085
146.32695	266.09961	266.09848	-0.00113
146.82526	266.98804	266.98667	-0.00137
146.89243	267.10791	267.10651	-0.00140
147.45616	268.11499	268.11334	-0.00165
147.94227	268.98486	268.98306	-0.00180
148.00072	269.08960	269.08775	-0.00185
148.01869	269.12183	269.11992	-0.00191
148.55936	270.09131	270.08919	-0.00212
148.58047	270.12915	270.12708	-0.00207
149.12320	271.10425	271.10186	-0.00239

149.14212	271.13818	271.13588	-0.00230
149.68590	272.11694	272.11440	-0.00254
150.24259	273.12085	273.11827	-0.00258
150.79594	274.12036	274.11781	-0.00255
151.33410	275.09448	275.09166	-0.00282
151.35677	275.13550	275.13272	-0.00278
151.88771	276.09814	276.09530	-0.00284
151.90492	276.12939	276.12654	-0.00285
152.43950	277.10059	277.09747	-0.00312
152.99030	278.10303	278.09970	-0.00333
153.01902	278.15527	278.15200	-0.00327
153.53925	279.10376	279.10035	-0.00341
153.57093	279.16162	279.15816	-0.00346
154.09410	280.11719	280.11361	-0.00358
154.57039	280.98877	280.98239	-0.00638
154.64501	281.12524	281.12152	-0.00372
155.11902	281.99414	281.99019	-0.00395
155.19108	282.12622	282.12236	-0.00386
155.72584	283.10840	283.10421	-0.00419
155.74355	283.14087	283.13677	-0.00410
156.27083	284.11108	284.10664	-0.00444
156.28983	284.14600	284.13831	-0.00769
156.81941	285.12207	285.11450	-0.00757
156.83922	285.15869	285.15105	-0.00764
157.29032	285.99146	285.98395	-0.00751
157.36650	286.13232	286.12472	-0.00760
157.88951	287.09961	287.09219	-0.00742
157.91072	287.13892	287.13147	-0.00745
158.42584	288.09326	288.08599	-0.00727
158.44952	288.13721	288.12991	-0.00730
158.97528	289.11304	289.10588	-0.00716
158.99834	289.15601	289.14873	-0.00728
159.51126	290.10986	290.10255	-0.00731
160.05092	291.11499	291.10780	-0.00719
160.58852	292.11816	292.11098	-0.00718
161.05546	292.99072	292.98239	-0.00833
161.11425	293.10083	293.09368	-0.00715
161.13026	293.13086	293.12363	-0.00723
161.63648	294.07861	294.07150	-0.00711
161.66612	294.13403	294.12704	-0.00699
162.17164	295.08228	295.07521	-0.00707
162.20441	295.14380	295.13674	-0.00706
162.72498	296.12207	296.11485	-0.00722
162.73041	296.14722	296.14012	-0.00710
163.25924	297.12769	297.12040	-0.00729
163.27709	297.16113	297.15403	-0.00710
163.78863	298.12573	298.11847	-0.00726
163.80737	298.16113	298.15383	-0.00730
164.30813	299.10693	299.09954	-0.00739
164.32601	299.14063	299.13334	-0.00729
164.83543	300.10449	300.09703	-0.00746
164.85552	300.14233	300.13346	-0.00887
165.36447	301.10693	301.09818	-0.00875
165.38969	301.15479	301.14601	-0.00878
165.89258	302.10938	302.10085	-0.00853
165.91550	302.15308	302.14420	-0.00888
166.42371	303.11938	303.11097	-0.00841
166.95167	304.12500	304.11674	-0.00826

167.40644	304.99243	304.98240	-0.01003
167.47879	305.13062	305.12259	-0.00803
168.00319	306.13281	306.12491	-0.00790
168.50264	307.08887	307.08110	-0.00777
168.51625	307.11499	307.10718	-0.00781
168.53286	307.14673	307.13900	-0.00773
169.02830	308.09692	308.08908	-0.00784
169.05465	308.14746	308.13964	-0.00782
169.55172	309.10205	309.09443	-0.00762
169.58294	309.16211	309.15443	-0.00768
170.08917	310.13599	310.12845	-0.00754
170.10385	310.16431	310.15671	-0.00760
170.61218	311.14380	311.13636	-0.00744
171.12881	312.14111	312.13358	-0.00753
171.63614	313.12207	313.11290	-0.00917
171.65452	313.15747	313.14848	-0.00899
172.14897	314.11499	314.10633	-0.00866
172.66685	315.11963	315.11113	-0.00850
173.18485	316.12598	316.11779	-0.00819
173.63064	316.99316	316.98542	-0.00774
173.70271	317.13354	317.12580	-0.00774
174.21804	318.13794	318.13050	-0.00744
174.65426	318.98950	318.97920	-0.01030
174.73429	319.14600	319.13859	-0.00741
175.24642	320.14746	320.14024	-0.00722
175.74640	321.12646	321.11964	-0.00682
175.76487	321.16284	321.15586	-0.00698
176.24974	322.11401	322.10716	-0.00685
176.27271	322.15894	322.15228	-0.00666
176.75777	323.11206	323.10543	-0.00663
176.77484	323.14551	323.13902	-0.00649
176.79025	323.17603	323.16932	-0.00671
177.25653	324.09351	324.08702	-0.00649
177.79673	325.15820	325.14936	-0.00884
180.73848	330.98779	330.97919	-0.00860
180.81864	331.14722	331.14070	-0.00652
181.32181	332.14990	332.14367	-0.00623
181.82791	333.16016	333.15404	-0.00612
182.32852	334.16064	334.15494	-0.00570
182.81787	335.14038	335.13483	-0.00555
182.83564	335.17603	335.17042	-0.00561
183.31132	336.12964	336.12437	-0.00527
186.71018	342.98511	342.97919	-0.00592
187.78081	345.15918	345.15564	-0.00354
192.57646	354.98462	354.97919	-0.00543
199.28839	368.97485	368.97885	0.00400
204.93816	380.96753	380.97600	0.00847
210.49833	392.96436	392.97599	0.01163
215.97201	404.96289	404.97599	0.01310
221.36523	416.96826	416.97600	0.00774



<u>distance</u>	<u>mass M<sub>1</sub></u>	<u>mass M<sub>2</sub></u>	<u>M<sub>2</sub>-M<sub>1</sub></u>
16.27832	85.00836	85.01141	0.00305
16.29874	85.02892	85.03194	0.00302
16.33458	85.06499	85.06798	0.00299
16.37078	85.10144	85.10439	0.00295
17.27587	86.01534	86.01715	0.00181
17.29669	86.03641	86.03821	0.00180
17.33350	86.07368	86.07544	0.00176
18.20960	86.96330	86.96404	0.00074
18.26948	87.02419	87.02486	0.00067
18.28856	87.04361	87.04427	0.00066
19.25678	88.03241	88.03203	-0.00038
20.23850	89.04068	89.03933	-0.00135
21.19699	90.03058	90.02836	-0.00222
21.21428	90.04848	90.04625	-0.00223
22.18501	91.05667	91.05364	-0.00303
23.11614	92.02896	92.02525	-0.00371
23.14902	92.06339	92.05966	-0.00373
24.03956	92.99829	92.99520	-0.00309
24.07661	93.03728	93.03294	-0.00434
24.11006	93.07249	93.06813	-0.00436
25.03052	94.04413	94.03923	-0.00490
25.06505	94.08067	94.07576	-0.00491
25.49712	94.53857	94.53344	-0.00513
25.94549	95.01492	95.00958	-0.00534
25.97000	95.04100	95.03564	-0.00536
25.98129	95.05302	95.04765	-0.00537
26.01576	95.08969	95.08431	-0.00538
26.92597	96.06073	96.05498	-0.00575
26.96030	96.09747	96.09169	-0.00578
27.83800	97.03867	97.03259	-0.00608
27.86565	97.06839	97.06231	-0.00608
27.90014	97.10547	97.09939	-0.00608
28.74810	98.01942	98.01312	-0.00630
28.80111	98.07669	98.07264	-0.00405
28.83424	98.11250	98.10843	-0.00407
29.67831	99.02693	99.02229	-0.00464
29.73095	99.08409	99.07942	-0.00467
29.76503	99.12111	99.11642	-0.00469
30.57002	99.99754	99.99238	-0.00516
30.60440	100.03506	100.02988	-0.00518
30.65724	100.09274	100.08753	-0.00521
31.49113	101.00511	101.00143	-0.00368
31.52600	101.04335	101.03770	-0.00565
32.44049	102.04886	102.04278	-0.00608
33.34238	103.04535	103.03894	-0.00641
33.35472	103.05902	103.05260	-0.00642
34.22968	104.03043	104.02376	-0.00667
34.24847	104.05135	104.04466	-0.00669
34.26207	104.06648	104.05980	-0.00668
35.09804	104.99901	104.99213	-0.00688
35.13166	105.03661	105.02972	-0.00689
35.16570	105.07466	105.06777	-0.00689
36.02958	106.04303	106.03599	-0.00704
36.05375	106.07019	106.06315	-0.00704
36.06447	106.08224	106.07520	-0.00704
36.47019	106.53864	106.53156	-0.00708
36.92600	107.05257	107.04543	-0.00714
36.95837	107.08911	107.08197	-0.00714



37.36238	107.54572	107.53859	-0.00713
37.81597	108.05952	108.05239	-0.00713
37.84872	108.09666	108.09142	-0.00524
38.24609	108.54788	108.54249	-0.00539
38.70218	109.06691	109.06137	-0.00554
38.73574	109.10516	109.09960	-0.00556
39.55397	110.03957	110.03378	-0.00579
39.58569	110.07588	110.07009	-0.00579
39.61748	110.11226	110.10647	-0.00579
40.41514	111.02731	111.02134	-0.00597
40.46475	111.08435	111.07837	-0.00598
40.49624	111.12056	111.11458	-0.00598
41.25747	111.99770	111.99360	-0.00410
41.28919	112.03435	112.02823	-0.00612
41.37030	112.12801	112.12190	-0.00611
42.12783	113.00481	112.99864	-0.00617
42.16050	113.04271	113.03653	-0.00618
42.24082	113.13589	113.12970	-0.00619
43.02596	114.04877	114.04257	-0.00620
43.88950	115.05704	115.05087	-0.00617
44.74638	116.06192	116.05582	-0.00610
45.54096	116.99760	116.99436	-0.00324
45.59304	117.05907	117.05579	-0.00328
45.60504	117.07324	117.06996	-0.00328
46.42577	118.04399	118.04043	-0.00356
46.45548	118.07919	118.07563	-0.00356
47.22611	118.99448	118.99069	-0.00379
47.26380	119.03932	119.03554	-0.00378
47.27386	119.05130	119.04752	-0.00378
47.30508	119.08847	119.08466	-0.00381
47.68747	119.54411	119.54023	-0.00388
48.06740	119.99770	120.99373	0.99603
48.11821	120.05841	120.05449	-0.00392
48.14628	120.09196	120.08799	-0.00397
48.93003	121.03073	121.02662	-0.00411
48.98963	121.10226	121.09815	-0.00411
49.76762	122.03801	122.03380	-0.00421
49.79745	122.07394	122.06975	-0.00419
50.60198	123.04555	123.04130	-0.00425
50.66226	123.11850	123.11425	-0.00425
51.38528	123.99519	123.99360	-0.00159
51.43280	124.05292	124.04867	-0.00425
51.49282	124.12585	124.12161	-0.00424
52.24407	125.04056	125.03634	-0.00422
52.32075	125.13411	125.12991	-0.00420
53.06823	126.04788	126.04376	-0.00412
53.14425	126.14101	126.13689	-0.00412
53.88783	127.05365	127.04965	-0.00400
53.96520	127.14879	127.14781	-0.00098
54.69597	128.04926	128.04806	-0.00120
54.70931	128.06572	128.06452	-0.00120
55.51486	129.06207	129.06067	-0.00140
55.54100	129.09445	129.09306	-0.00139
56.32016	130.06195	130.06041	-0.00154
56.33436	130.07962	130.07809	-0.00153
57.06663	130.99226	130.99060	-0.00166
57.11287	131.05000	131.04833	-0.00167
57.13303	131.07516	131.07351	-0.00165

57.14297	131.08757	131.08593	-0.00164
57.50662	131.54214	131.54045	-0.00169
57.86868	131.99551	131.99536	-0.00015
57.88916	132.02118	132.01945	-0.00173
57.91733	132.05650	132.05475	-0.00175
57.94528	132.09152	132.08979	-0.00173
58.67435	133.00716	133.00537	-0.00179
58.69099	133.02808	133.02631	-0.00177
58.71867	133.06291	133.06114	-0.00177
58.74876	133.10078	133.09901	-0.00177
59.51845	134.07118	134.06941	-0.00177
59.54816	134.10872	134.10694	-0.00178
60.28754	135.04436	135.04262	-0.00174
60.31562	135.07994	135.07822	-0.00172
60.34218	135.11363	135.11189	-0.00174
61.08051	136.05142	136.04977	-0.00165
61.10893	136.08759	136.08593	-0.00166
61.13760	136.12407	136.12243	-0.00164
61.82457	136.99979	136.99823	-0.00156
61.85426	137.03770	137.03614	-0.00156
61.92773	137.13153	137.12999	-0.00154
62.64199	138.04546	138.04404	-0.00142
63.42715	139.05359	139.05340	-0.00019
63.49968	139.14691	139.14670	-0.00021
64.20723	140.05884	140.05852	-0.00032
64.98892	141.06981	141.06936	-0.00045
65.76352	142.07518	142.07468	-0.00050
66.46672	142.99100	142.99200	0.00100
66.53483	143.07986	143.07929	-0.00057
67.23717	143.99776	143.99720	-0.00056
67.28155	144.05586	144.05529	-0.00057
67.30790	144.09036	144.08980	-0.00056
68.00585	145.00574	145.00519	-0.00055
68.04937	145.06291	145.06237	-0.00054
68.81414	146.06944	146.06896	-0.00048
69.48886	146.96037	146.95995	-0.00042
69.54068	147.02892	147.02910	0.00018
69.55080	147.04230	147.04250	0.00020
69.57806	147.07835	147.07857	0.00022
70.26755	147.99194	147.99253	0.00059
70.28456	148.01453	148.01513	0.00060
70.31128	148.04997	148.05061	0.00064
70.33843	148.08603	148.08666	0.00063
70.36586	148.12244	148.12309	0.00065
71.00255	148.96895	148.96998	0.00103
71.04044	149.01941	149.02046	0.00105
71.06888	149.05728	149.05836	0.00108
71.08969	149.08501	149.08608	0.00107
71.09747	149.09537	149.09646	0.00109
71.12300	149.12936	149.13047	0.00111
71.76640	149.98772	149.98923	0.00151
71.79408	150.02470	150.02624	0.00154
71.81012	150.04614	150.04768	0.00154
71.82411	150.06483	150.06639	0.00156
72.51984	150.99600	150.99823	0.00223
72.54298	151.02704	151.02908	0.00204
72.56247	151.05318	151.05522	0.00204
72.63178	151.14610	151.14821	0.00211

73.31214	152.05997	152.06256	0.00259
74.05841	153.06552	153.06868	0.00316
74.80398	154.07346	154.07722	0.00376
75.47918	154.98912	154.99343	0.00431
75.52109	155.04604	155.05040	0.00436
75.54812	155.08275	155.08714	0.00439
76.28775	156.08922	156.09424	0.00502
77.00025	157.06183	157.06754	0.00571
77.02557	157.09645	157.10189	0.00544
77.73613	158.06956	158.07488	0.00532
78.46986	159.07756	159.08278	0.00522
78.49606	159.11362	159.11884	0.00522
79.20151	160.08589	160.09106	0.00517
79.92974	161.09268	161.09780	0.00512
80.57549	161.98808	161.99040	0.00232
80.61540	162.04350	162.04862	0.00512
81.29984	162.99544	163.00055	0.00511
81.34007	163.05148	163.05660	0.00512
82.06242	164.05934	164.06448	0.00514
82.78364	165.06874	165.07393	0.00519
83.49996	166.07436	166.07961	0.00525
84.15031	166.99001	166.99893	0.00892
84.18059	167.03270	167.04160	0.00890
84.21425	167.08017	167.08904	0.00887
84.90434	168.05479	168.06314	0.00835
84.92970	168.09067	168.09898	0.00831
85.55222	168.97240	168.98026	0.00786
85.56493	168.99042	168.99828	0.00786
85.61582	169.06261	169.07042	0.00781
85.64118	169.09859	169.10638	0.00779
86.25509	169.97072	169.97807	0.00735
86.26947	169.99117	169.99216	0.00099
86.35027	170.10612	170.11342	0.00730
87.03273	171.07867	171.08547	0.00680
87.65624	171.96964	171.97602	0.00638
87.73762	172.08609	172.09242	0.00633
88.44110	173.09447	173.10035	0.00588
89.06353	173.98912	173.99462	0.00550
89.76276	174.99692	175.00200	0.00508
90.49860	176.06065	176.06529	0.00464
91.19292	177.06732	177.07157	0.00425
91.88743	178.07715	178.08102	0.00387
91.90221	178.09868	178.10817	0.00949
92.51410	178.99081	178.99963	0.00882
92.57780	179.08382	179.09257	0.00875
93.24360	180.05736	180.06538	0.00802
93.26685	180.09140	180.09939	0.00799
93.87892	180.98878	180.98880	0.00002
93.92828	181.06126	181.06856	0.00730
93.95413	181.09921	181.10649	0.00728
94.56131	181.99193	181.99856	0.00663
94.61461	182.07040	182.07698	0.00658
94.64040	182.10838	182.11492	0.00654
95.24809	183.00432	183.01025	0.00593
97.26288	185.99066	185.99457	0.00391
97.31469	186.06776	186.06695	-0.00081
97.93819	186.99704	186.99608	-0.00096
99.32448	189.07149	189.07028	-0.00121

99.99251	190.07524	190.07393	-0.00131
100.66373	191.08647	191.08509	-0.00138
101.33085	192.09419	192.09273	-0.00146
101.92259	192.99030	192.98880	-0.00150
101.99558	193.10097	193.09945	-0.00152
102.58496	193.99583	193.99426	-0.00157
102.65903	194.10843	194.10686	-0.00157
103.24833	195.00551	195.00391	-0.00160
103.29818	195.08148	195.07988	-0.00160
103.95857	196.08945	196.08783	-0.00162
106.49672	199.98775	199.98616	-0.00159
107.14928	200.99625	200.99503	-0.00122
107.84790	202.07874	202.07712	-0.00162
108.49510	203.08417	203.08254	-0.00163
109.13817	204.08566	204.08404	-0.00162
109.71763	204.99022	204.98861	-0.00161
109.78055	205.08856	205.08695	-0.00161
110.42257	206.09337	206.09177	-0.00160
112.33111	209.09494	209.09347	-0.00147
114.15750	211.98776	211.98720	-0.00056
114.79024	212.99463	212.99327	-0.00136
116.10016	215.08669	215.08532	-0.00137
116.72709	216.09158	216.09024	-0.00134
117.28637	216.99005	216.98955	-0.00050
117.34925	217.09117	217.09067	-0.00050
117.97449	218.09805	218.09743	-0.00062
118.52512	218.98671	218.98601	-0.00070
118.59847	219.10522	219.10450	-0.00072
119.14511	219.98950	219.98869	-0.00081
121.05857	223.09889	223.09784	-0.00105
121.60276	223.98723	223.98720	-0.00003
121.67221	224.10072	224.09961	-0.00111
122.21890	224.99515	224.99399	-0.00116
122.87881	226.07719	226.07599	-0.00120
124.10388	228.09286	228.09159	-0.00127
124.64695	228.98929	228.98849	-0.00080
124.71405	229.10017	229.09938	-0.00079
125.32260	230.10703	230.10613	-0.00090
125.85327	230.98683	230.98560	-0.00123
126.45679	231.98949	231.98845	-0.00104
126.51596	232.08791	232.08686	-0.00105
127.06450	233.00130	233.00019	-0.00111
128.85044	235.98769	235.98639	-0.00130
129.44983	236.99425	236.99292	-0.00133
130.69135	239.08601	239.08461	-0.00140
131.81613	240.98909	240.98758	-0.00151
132.99220	242.98708	242.98560	-0.00148
133.58080	243.99016	243.98871	-0.00145
134.17313	245.00168	245.00026	-0.00142
134.81692	246.10349	246.10211	-0.00138
135.39880	247.10149	247.10013	-0.00136
135.91454	247.98773	247.98641	-0.00132
137.65665	250.99321	250.99183	-0.00138
138.29225	252.09428	252.09309	-0.00119
138.87196	253.10066	253.09950	-0.00116
139.45017	254.10643	254.10533	-0.00110
139.95539	254.98691	254.98584	-0.00107
142.70951	259.81348	259.81281	-0.00067

143.93941	261.98364	261.98299	-0.00065
144.00441	262.09863	262.09794	-0.00069
144.50893	262.99170	262.99183	0.00013
146.75506	266.98633	266.98561	-0.00072
147.39229	268.12500	268.12490	-0.00010
147.87181	268.98364	268.98345	-0.00019
150.64933	273.98389	273.98400	0.00011
151.20627	274.99219	274.99199	-0.00020
152.94521	278.15210	278.15206	-0.00004
153.40273	278.98657	278.98629	-0.00028
153.49589	279.15674	279.15637	-0.00037
154.49482	280.98364	280.98239	-0.00125
155.04155	281.98608	281.98608	0.0
155.59235	282.99780	282.99794	0.00014
157.21265	285.98462	285.98517	0.00055
159.90571	290.98438	290.98519	0.00081
160.97564	292.98267	292.98239	-0.00028
161.51047	293.98438	293.98555	0.00117
163.63556	297.98120	297.98324	0.00204
165.22377	300.98633	300.98808	0.00175
167.32226	304.98022	304.98240	0.00218
171.48577	312.98389	312.98863	0.00474
173.54315	316.97778	316.98189	0.00411
174.56674	318.97437	318.97920	0.00483
177.62797	324.98389	324.98861	0.00472
179.64705	328.97900	328.98328	0.00428
180.65218	330.97705	330.97919	0.00214
181.15553	331.97998	331.98379	0.00381
186.62469	342.97705	342.97919	0.00214
186.63254	342.99292	342.99538	0.00246
187.11962	343.98145	343.98373	0.00228
192.49369	354.98242	354.97919	-0.00323
198.25762	366.97900	366.97920	0.00020
199.20708	368.97461	368.97980	0.00519
203.92517	378.97461	378.98692	0.01231
204.86007	380.97266	380.97600	0.00334
205.32839	381.97534	381.98561	0.01027
210.41350	392.95166	392.96553	0.01387
210.42240	392.97095	392.97599	0.00504
215.89732	404.96802	404.97599	0.00797
221.29113	416.96948	416.97600	0.00652

FORTRAN IV G LEVEL 21

MAIN

```
REAL * 8 X,Y,DIFF,SUMDIF,SUMDD,AMEAN,SD
```

```
1 FORMAT(1H1)
```

```
2 FORMAT(2F10.5)
```

```
3 FORMAT(1H,30X,3(3X,F10.5))
```

```
4 FORMAT(19H1MEAN DIFFERENCE = ,E11.4/19H S.D. OF ,, = ,E11.4)
```

```
SUMDD=0
```

```
SUMDIF=0
```

```
N=0
```

```
WRITE(6,1)
```

```
5 READ(5,2,END=6)X,Y
```

```
N=N+1
```

```
DIFF=Y-X
```

```
SUMDIF=SUMDIF+DIFF
```

```
SUMDD=SUMDD+DIFF * DIFF
```

```
WRITE(6,3)X,Y,DIFF
```

```
IF(MOD(N,58) .EQ. 0) WRITE(6,1)
```

```
GOTO 5.
```

```
6 AMEAN=SUMDIF/N
```

```
SD=DSQRT((SUMDD-SUMDIF * SUMDIF/N)/(N-1))
```

```
12 FORMAT(1H ,30X,15HNO. OF PAIRS = ,I8)
```

```
WRITE(6,4)AMEAN,SD
```

```
WRITE(6,12) N
```

```
CALL EXIT
```

```
END
```

TABLE 2.6

Coal Extraction Fraction	Mean Difference (Millimass Units)	Standard Deviation (Millimass Units)	Number of pairs used for each calculation
E	-2.398	+ 27.76	605
F	+ 1.001	+ 4.40	884
G	- 0.699	+ 5.27	933
H	- 3.344	+ 5.14	456
L	+ 2.607	+ 54.93	331

#### 2.4. Discussion of Results.

Examination of tables 2.1 - 2.6 reveals that for all the coal extraction samples studied, the difference between the masses calculated by two different methods is rarely higher than about  $10^{-3}$  mass units and in many cases is as low as  $10^{-4}$  -  $10^{-5}$  mass units. Thus the results given by the spline-fit interpolation method seem to be very close to the results given by the variation of the Biemann method. However the advantages of the spline-fit interpolation method are quite substantial.

Firstly, for this method, an internal standard compound is not always necessary for the calculation of the masses of the ions. As long as the masses of five ions are known, this is sufficient for the construction of the spline, even over such a wide mass range as from 80 to 400, and the subsequent interpolation of all the other unknown peaks. In most samples it is not usually difficult to identify five masses in the spectrum spaced sufficiently well apart that the unknown peaks lie among these five. In cases where none, or only some, of these five mass peaks can be identified, and it is difficult to obtain a suitable reference compound, some of these reference masses can be calculated by the peak matching technique on a Nier-Johnson geometry mass spectrometer. Though this technique is tedious and time consuming, it is not difficult to carry out for five peaks or less.

Secondly, this method can be used in any mass spectrometer with an electrical or photographic recording system. In the case of the photographic recording system used here, the distances required for the calculations were obtained by measurement with a very accurate comparator. If an electrical recording of the mass peaks is made, there need be no loss of accuracy provided that an attachment to the spectrometer is available which accurately marks the distances on the paper chart.

In the Biemann mathematical interpolation, and most of the other computerised methods used in mass spectrometry, the interpolation or



extrapolation is made stepwise and the degree of error increases according to the number of approximations. In the method employed here, interpolation is made in one step.

The flexibility of this method is important and, moreover, it does not require sophisticated systems and computer programmes for its application.

It is felt that this new mathematical method of calculating the masses of the ions in the spectrum offers an advantage over the other methods, previously mentioned, both in its simplicity and in its rapidity.

Bibliography (Chapter 2).

1. J.H. Beynon, Nature, Lond., 1954, 174, 735.
2. J.H. Beynon, Mikrochim. Acta, 1956, 437.
3. F.W. McLafferty, Appl. Spect., 1957, 11, 148.
4. J.H. Beynon, "Mass Spectrometry and its Applications to Organic Chemistry," Elsevier Publishing Co., Amsterdam, 1960, p.28-57.
5. J.H. Beynon in "Advances in Mass Spectrometry," Vol.I, Ed. J.D. Waldron, The Institute of Petroleum, London, 1959, p.328.
6. J.T. Kerr and H.E. Duckworth, Can. J. Phys., 1958, 36, 986.
7. H.E. Duckworth, J.T. Kerr and G.R. Bainbridge, "Nuclear Masses and their Determination," Pergamon Press Ltd., London, 1958.
8. J.T. Kerr, G.R. Bainbridge, J.W. Dewdney and H.E. Duckworth in Reference 5, p.1.
9. J.H. Beynon in "Advances in Mass Spectrometry," Vol.II, Ed. R.M. Elliott, The Institute of Petroleum, London, 1963, p.216.
10. K.S. Quisenberry, T.T. Scolman and A.O. Nier, Phys. Rev., 1956, 102, 1071.
11. A.O. Nier, Phys. Rev., 1951, 81, 624.
12. Associated Electrical Industries Operation Manual for the MS9.
13. R.D. Craig, B.N. Green and J.D. Waldron, Chima, 1963, 17, 33.
14. H.M. Fales, R. Binks, M. Elliott and R. Freeman, 14th Ann. Conf. on Mass Spect., Dallas, May, 1966, p.625.
15. W.A. Wolstenholme, 4th Ann. MS9 Mass Spectrometer Users Conf., Manchester, 1966.
16. J.H. Beynon, R.A. Saunders and A.E. Williams, Analyt. Chem., 1961, 33, 221.
17. K. Biemann, W. McMurray and P. Bommer, 12th Ann. Conf. on Mass Spect., Montreal, 1964, p.442.
18. P. Bommer, W. McMurray and K. Biemann in Reference 17, p.428.

19. D.M. Desiderio and K. Biemann in Reference 17, p.433.
20. K. Biemann, P. Bommer, D.M. Desiderio and W.J. McMurray in "Advances in Mass Spectrometry," Vol.III, Ed. W.L. Mead, The Institute of Petroleum, London, 1966, p.639.
21. K. Biemann, Pure and Appl. Chem., 1964, 2, 95.
22. E. Kendrick, Analyt. Chem., 1963, 35, 2146.
23. W.K. Reid, W.L. Mead and A.R. West, Analyt. Chem., 1964, 36, 1140.
24. J.H. Beynon and A.E. Williams, "Mass and Abundance Tables for use in Mass Spectrometry," Elsevier Publishing Co., Amsterdam, 1963.
25. K. Biemann, P. Bommer and D.M. Desiderio, Tetrahedron Lett., 1964, 2, 1725.
26. K. Biemann and P.V. Fennessey, Chima, 1967, 21, 226.
27. A.L. Burlingame in Reference 20, p.701.
28. R.W. Olsen, 13th Ann. Conf. On Mass Spect., St. Louis, May, 1965, p.191.
29. (a) R. Venkataraghavan, F.W. McLafferty and J.W. Amy, Analyt. Chem., 1967, 39, 178.  
(b) R. Venkataraghavan, R.D. Board, R. Klimowski, J.W. Amy and F.W. McLafferty in "Advances in Mass Spectrometry," Vol.IV, Ed. E. Kendrick, The Institute of Petroleum, London, 1968, p.65.
30. K. Biemann, 11th Ann. Conf. on Mass Spect., San Francisco, May, 1963, p.235.
31. D.D. Tunnicliff and P.A. Wadsworth, Analyt. Chem., 1968, 40, 1826.
32. C. Cone, P. Fennessey, R. Hites, N. Mancuso and K. Biemann, 15th Ann. Conf. on Mass Spect., Denver, May, 1967, p.114.
33. K. Biemann and P.V. Fennessey in Reference 14, p.322.
34. D.M. Desiderio and T.E. Mead, Analyt. Chem., 1968, 40, 2090.
35. D.M. Desiderio, T.E. Mead, 16th Ann. Conf. On Mass Spect., Pittsburgh, May, 1968, p.125.

36. C. Merritt, P. Issenberg, M.L. Bazinet, B.N. Green, T.O. Merren and J.G. Murray, *Analyt. Chem.*, 1965, 37, 1037.
37. P. Issenberg, M.L. Bazinet and C. Merritt, *Analyt. Chem.*, 1965, 37, 1074.
38. W.J. McMurray, B.N. Green and S.R. Lipsky, *Analyt. Chem.*, 1966, 38, 1194.
39. B.N. Green, T.O. Merren and J.G. Murray, in Reference 28, p.204.
40. R.W. Olsen and A.L. Burlingame in Reference 28, p.192.
41. H.C. Bowen, T. Chenevix-Trench, S.D. Drackley, R.C. Faust and R.A. Saunders, *J. Sci. Instr.*, 1967, 44, 343.
42. H.C. Bowen, D. Clayton, D.J. Shields and H.M. Stanier in "Advances in Mass Spectrometry," Vol.IV, Ed. E. Kendrick, The Institute of Petroleum, London, 1968, p.257.
43. W.J. McMurray, S.R. Lipsky and B.N. Green in Reference 42, p.77.
44. W.J. McMurray, S.R. Lipsky and B.N. Green in Reference 32, p.82.
45. C. Merritt, P. Issenberg, M.L. Bazinet, B.N. Green, T.O. Merren and J.G. Murray in Reference 42, p.55.
46. A.L. Burlingame, R.W. Olsen and D.H. Smith in Reference 32, p.568.
47. A.L. Burlingame, D.H. Smith and R.W. Olsen, *Analyt. Chem.*, 1968, 40, 13.
48. A.L. Burlingame, D.H. Smith, T.O. Merren and R.W. Olsen in Reference 35, p.109.
49. A.L. Burlingame in Reference 42, p.15.
50. D.H. Smith, R.W. Olsen and A.L. Burlingame in Reference 35, p.101.
51. T. Aczel, D.E. Allan, J.H. Harding and E.A. Knipp in Reference 35, p.366.
52. B.H. Johnson and T. Aczel, *Analyt. Chem.*, 1967, 39, 682.
53. T. Aczel, D.E. Allan, J.H. Harding and E.A. Knipp, *Analyt. Chem.*, 1970, 42, 341.

54. R. Venkataraghavan, R. Klimowski and F.W. McLafferty, *Accounts Chem. Res.*, 1970, 3, 158.
55. Several papers in "Advances in Mass Spectrometry," Vol.IV, Ed. E. Kendrick, The Institute of Petroleum, London, 1968.
56. K. Biemann, *Z. Analyt. Chem.*, 1968, 235, 75.
57. T. Komori, T. Kawasaki, T. Aoyama, M. Shino, M. Togashi and M. Arai in "Recent Developments in Mass Spectroscopy," Proc. Int. Conf. Mass Spectroscopy, Kyoto, Ed. K. Ogata and T. Hayakawa, University of Tokyo Press, Kyoto, 1970, p.281.
58. R.D. Board, PhD Thesis, Purdue University, 1968.
59. A.L. Burlingame, D.H. Smith, T.O. Merren and R.W. Olsen in "Computers in Analytical Chemistry," Ed. C.H. Orr and J.A. Norris (Progress in Analyt. Chem. Ser., Vol.IV), Plenum Press, New York, 1970, p.17.
60. A.L. Burlingame in Reference 57, p.104.
61. R.J. Klimowski, R. Venkataraghavan and F.W. McLafferty, *Org. Mass Spect.*, 1970, 4, 17.
62. D.H. Smith, R.W. Olsen, F.C. Walls and A.L. Burlingame, *Analyt. Chem.*, 1971, 43, 1796.
63. C.J. Eckhardt and M.L. Gross, *Int. J. Mass Spect. and Ion Phys.*, 1970, 5, 223.
64. R.H. Pennington, "Computer Methods and Numerical Analysis," MacMillan Co., London, 1971, Chapters 11 and 12.

### Chapter 3.

#### The Shape of Mass Spectral Peaks

##### 3.1. Introduction

The mass spectrum of a sample displays in a graphical or tabular form the measured mass-to-charge ratios of the separated ions and their corresponding intensities. Knowledge of the mass-to-charge ratios of the ions allows the determination of which species are present, while the measured ion intensities reveal how much of each is present.

The terms "ion abundance" or "ion intensity" refer to the number of ions detected in each separated ion beam. A very early method of detecting ions involved actual counting with the aid of a screen made of zinc sulphide which fluoresces when bombarded by ions.

The determination of ion abundance is very important in providing information about the relative quantities of isotopes. This information is applied in many fields, such as in the determination of isotopic constitution of the elements, in geochronometry, in biochemical processes and in the study of trace impurities in solids. In trace analytical applications the sensitivity limit of the instrument and the magnitude of the abundance sensitivity is of great importance.

Another application of ion abundance data is in finding the cracking pattern of a pure substance. The various peaks of the cracking pattern are usually expressed as percentages of the largest peak of the spectrum or as percentage of the sum of the relative intensities of all peaks considered in the spectrum. It is sometimes necessary to remove the contributions due to machine background by subtracting the intensities of the various peaks in the background spectrum from the intensities of the corresponding peaks in the sample spectrum. The sample spectrum is then normalised. The properties of mass spectral patterns can be used in qualitative identifications,

quantitative analysis and high temperature chemistry.

The first measurements of the relative isotopic abundances of the elements were made by Aston<sup>1</sup> in his mass spectrograph. Measurement of the relative abundances of ions in mass spectra was accomplished by Thomson<sup>2</sup>.

In current work, ion abundances are measured by either electrical or photographic techniques. The former measure the intensity of the ion current caused by the ions arriving at a collector; the latter utilise the fact that the darkening of certain photographic emulsions is proportional to the number of impinging ions. In both methods there are defects which may give rise to random and systematic errors in the determination of abundance measurements<sup>3</sup>.

In some treatments, the maximum height is taken as a measure of ion abundance; in others the intensities are based on peak areas. When peak areas have been used, the observed error has been in remarkable agreement with that predicted. The errors using peak heights tend to be slightly larger<sup>4</sup>.

In this work a method of calculating the ion abundance based upon peak area determinations was developed for slow scans.

### 3.2. Theory

The usual form of a spectrum is a series of peaks rising from a more or less uniform base line. The precise shape of each peak has given rise to some discussion. In the single-focusing instrument the ion beam is roughly of the flat-topped shape. This does not seem to be true of the double-focusing AEI MS9 mass spectrometer and, furthermore, the peak shape may well differ for different scanning speeds. At low scan speeds Carrick<sup>5</sup> has assumed that the peak shape is triangular to a good approximation. This triangular form is the result of the convolution of a "rectangular" cross-section ion beam (generated by the source slit) with a rectangular detector slit. Even under fast scanning conditions, the basic assumption of a triangular peak distorted by the finite bandwidth of the spectrometer's recording system is a close approximation to the actual output waveform<sup>6</sup>. Other workers have assumed that the peak is gaussian in shape<sup>7</sup> or of sinusoidal shape<sup>8</sup>.

An alternative analysis is made in the present work to prove Carrick's assumption of triangular shape.

The ion beam is represented by the function:

$$G(f) = AL \left\{ \frac{\sin Lf/2}{Lf/2} \right\}^2$$

where  $f$  is the frequency of the waveform and  $L$  and  $A$  are defined as shown in figure 3.1.

While this is formally distinct from the gaussian shape it is not too different from the probable shape of the ion beam for two reasons.

Most mass spectrometers have inbuilt circuitry which prevents the trace falling below the base line, and the lobes of the waveform adjacent to the principal lobe may be made insignificant in slow scans.

A single transient triangular pulse  $g(t)$  may be considered which is fully defined by two parameters,  $A$  and  $L$ , where  $A$  is the height and  $2L$  is the base of the triangle as shown in figure 3.2.



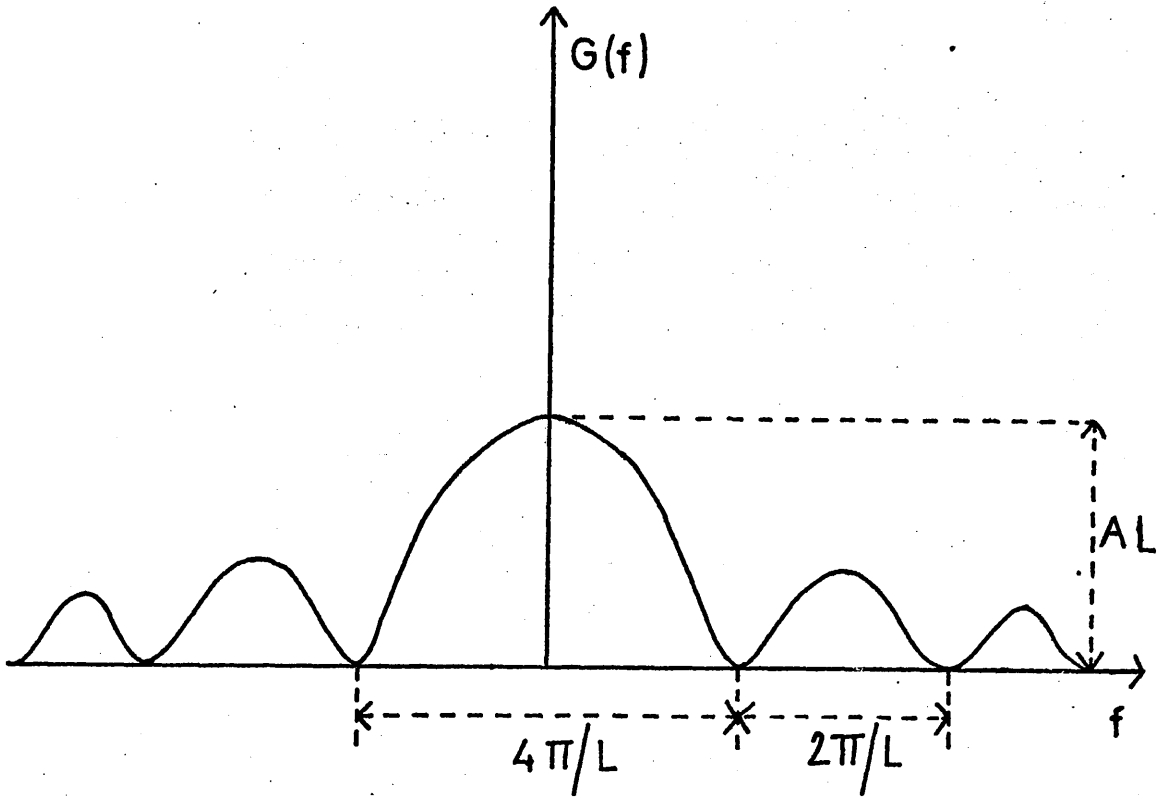


Fig. 3.1

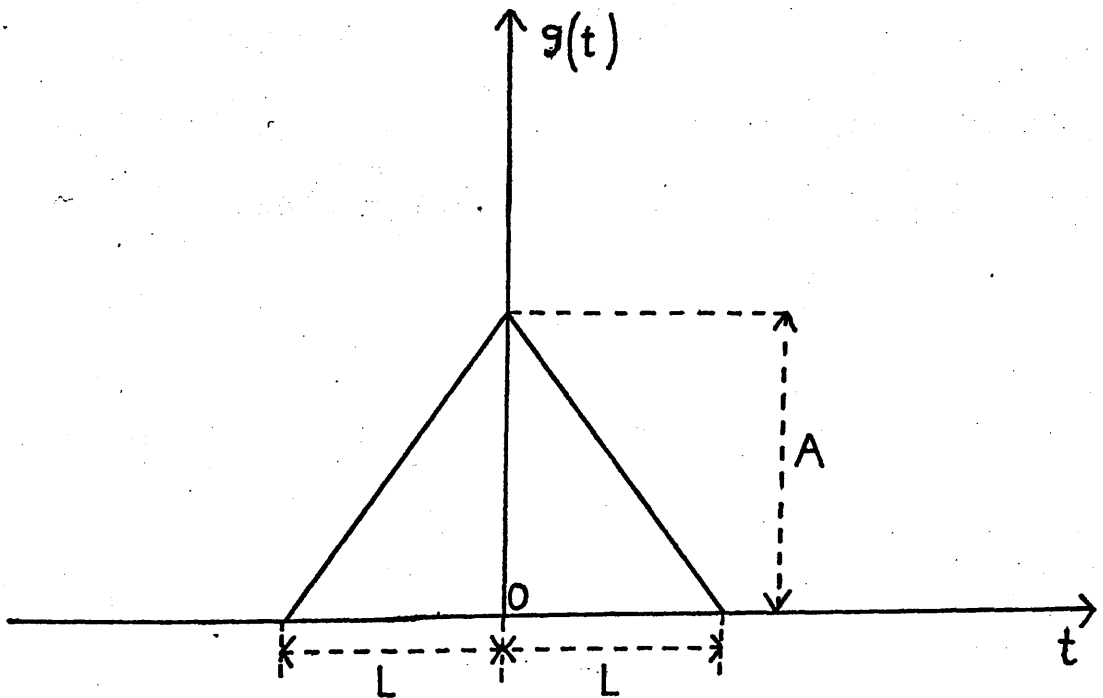


Fig. 3.2

In this:

$$g(t) = A \left( 1 - \frac{|t|}{L} \right) \begin{cases} |t| < L \\ |t| > L \end{cases}$$

and,  $g(t) = 0$

On carrying out the Fourier transform<sup>9</sup>, this function can be related to the frequency function  $G(f)$ . The amount of data contained in  $G(f)$  is precisely equivalent to that contained in  $g(t)$ ; the latter is in the time domain whilst the former represents the same information in the frequency and phase domain. This follows because the Fourier transforms  $g(t) \rightarrow G(f)$  and  $G(f) \rightarrow g(t)$  are one-to-one transformations and therefore no loss of information is involved<sup>10</sup>.

The transform of  $g(t) \rightarrow G(f)$ <sup>9</sup> is as follows.

$$\begin{aligned} G(f) &= \int_{-\infty}^{+\infty} g(t) e^{-itf} dt = \int_{-\infty}^{+\infty} A \left( 1 - \frac{|t|}{L} \right) e^{-itf} dt \\ &= \frac{A}{L} \int_{-L}^0 (L+t) e^{-itf} dt + \frac{A}{L} \int_0^{+L} (L-t) e^{-itf} dt \\ &= \frac{A}{L(if)^2} \left[ e^{-ifL} + e^{+ifL} - 2 \right]. \end{aligned}$$

Making  $x = fL/2$ ,

$$\text{then, } G(f) = AL \frac{\sin^2 x}{x^2} = AL \left\{ \frac{\sin fL/2}{fL/2} \right\}^2.$$

It is therefore apparent that a peak in the double-focusing mass spectrometer can be represented equally well by a function  $G(f)$  or a triangular function  $g(t)$ .

Thus, instead of measuring the area under the peak with a planimeter, as for a curve, the peak area may simply be calculated as that of an isosceles triangle.

### 3.3. Experimental and Results

The theory has been tested by running several samples on the Associated Electrical Industries Ltd. (AEI) MS902S, the double-focusing mass spectrometer. The source and collector slits were adjusted until a reasonable approximation to a triangular waveform was obtained under slow scan conditions. The samples, introduced through the cold inlet system, were run at a scan speed of 19 minutes per decade, at a chart speed of  $1.5 \text{ cms}^{-1}$  and with a bandwidth of  $5 \text{ cs}^{-1}$ . All samples were examined under standard conditions of electron energy of 70 eV, ion accelerating voltage of 8 kV, ion source temperature around  $100^{\circ}\text{C}$ , trap current 500  $\mu\text{A}$ , pressure of the order of  $10^{-6}$  torr\*. The spectra were recorded on a paper chart by a Honeywell 2106 ultraviolet galvanometer recorder.

The areas under the peaks were calculated both using a Stanley Allbrit zero-setting compensating polar planimeter and by the triangle method.

The results were compared for peaks in each spectrum at different sensitivities on the chart.

In order to avoid the need to measure the total height of the peak and the total base width for calculation of the triangular area, a mathematical expression requiring three measurements was developed. This gives greater accuracy since the extremities of the peak are not always well defined.

---

\*  $1 \text{ torr} = 1.333 \times 10^2 \text{ Nm}^{-2}$  (S.I. Units).

For an isosceles triangle:

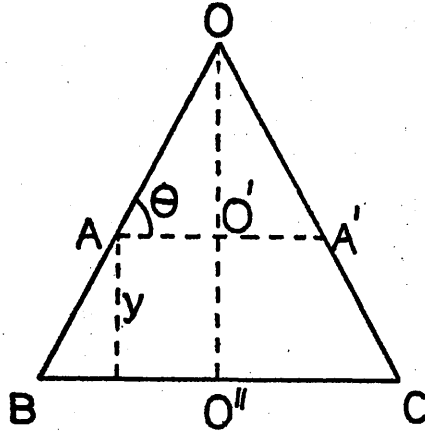


Fig. 3.3

it is possible to calculate the area if the following parameters associated with any point A along  $\overline{OB}$  are known.

$\overline{AA'}$  - distance from A to a symmetrical point A' .

$\theta$  - angle between  $\overline{OA}$  and  $\overline{AA'}$  .

$y$  - distance from A to the base  $\overline{BC}$  of the triangle.

Then, since

$$\text{area of triangle } \widehat{OAA'} = \frac{\overline{OO'} \cdot \overline{AA'}}{2}$$

and

$$\tan \theta = \frac{\overline{OO'}}{\overline{O'A}} = \frac{\overline{OO'}}{\frac{\overline{AA'}}{2}},$$

therefore

$$\overline{OO'} = \frac{\tan \theta \cdot \overline{AA'}}{2}$$

and

$$\text{area of triangle } \widehat{OAA'} = \frac{\tan \theta \cdot \overline{AA'}^2}{4} .$$

Also,

$$\overline{OO''} = y + \overline{OO'} = y + \frac{\tan \theta \cdot \overline{AA'}}{2}$$

and since

$$\frac{\text{Area of triangle } \widehat{OBC}}{\text{Area of triangle } \widehat{OAA'}} = \frac{\overline{OO''}^2}{\overline{OO'}^2},$$

then

$$\text{Area of triangle } \widehat{OBC} = \frac{\text{Area of triangle } \widehat{OAA'} \cdot \overline{OO''}^2}{\overline{OO'}^2}$$

$$\begin{aligned} &= \frac{\frac{\tan \theta \cdot \overline{AA'}^2}{4} \left( y + \frac{\tan \theta \cdot \overline{AA'}}{2} \right)^2}{\left( \frac{\tan \theta \cdot \overline{AA'}}{2} \right)^2} \\ &= \frac{(2y + \tan \theta \cdot \overline{AA'})^2}{4 \tan \theta} \end{aligned}$$

Hence,

$$\text{Area of triangle } \widehat{OBC} = \frac{(2y + \tan \theta \cdot \overline{AA'})^2}{4 \tan \theta} .$$

The areas of the peaks calculated by both the planimeter and the triangular formula for several compounds analysed in slow scan conditions are shown in tables 3.1 - 3.11. In addition, the error expressed as the difference between the two measurements is also shown in the same tables. The mean error and the standard deviation were also calculated by a computer programme and are as follows:

$$\text{Mean Difference} = - 0.03264 ,$$

$$\text{Standard Deviation} = + 0.213 ,$$

$$\text{Number of pairs} = 174.$$

In the following tables, the first column lists the area  $A_1$  in  $\text{cm}^2$  calculated using the planimeter, the second lists the area  $A_2$  in  $\text{cm}^2$  calculated using the triangular formula and the third lists the difference between  $A_2$  and  $A_1$ .

TABLE 3.1.

BENZENE	Area 1	Area 2	Difference
	5.25000	5.03000	-0.22000
	5.50000	4.90000	-0.60000
	1.90000	2.10000	0.20000
	1.90000	1.86000	-0.04000
	6.00000	5.50000	-0.50000
	1.00000	1.15000	0.15000
	1.25000	1.24000	-0.01000
	1.00000	1.20000	0.20000
	1.00000	0.94000	-0.06000
	1.22000	1.25000	0.03000
	1.75000	1.30000	-0.45000
	4.50000	4.95000	0.45000
	2.00000	1.96000	-0.04000
	2.75000	2.50000	-0.25000
	1.50000	1.40000	-0.10000
	1.50000	1.55000	0.05000
	1.25000	1.20000	-0.05000
	3.50000	3.50000	0.00
	1.25000	1.27000	0.02000
	3.75000	3.70000	-0.05000
	1.50000	1.70000	0.20000
	5.25000	5.10000	-0.15000

-----

Note - The computer output is printed to five decimal places, but only the first two decimal places should be taken as significant.

TABLE 3.2.

TOLUENE	Area 1	Area 2	Difference
	0.75000	0.78000	0.03000
	1.75000	1.66000	-0.09000
	3.25000	3.70000	0.45000
	1.00000	0.90000	-0.10000
	0.75000	0.90000	0.15000
	1.25000	1.05000	-0.20000
	0.50000	0.60000	0.10000
	1.50000	1.50000	0.00
	0.70000	0.70000	0.00
	1.00000	1.19000	0.19000
	0.50000	0.48000	-0.02000
	1.00000	0.90000	-0.10000
	1.30000	1.29000	-0.01000
	3.50000	3.40000	-0.10000

TABLE 3.3.

PERFLUOROKEROSENE	Area 1	Area 2	Difference
	1.20000	1.00000	-0.20000
	0.50000	0.50000	0.00
	1.45000	1.40000	-0.05000
	1.75000	1.71000	-0.04000
	1.75000	1.51000	-0.24000
	2.50000	2.40000	-0.10000
	1.25000	1.00000	-0.25000
	2.50000	2.01000	-0.49000
	1.60000	1.50000	-0.10000
	1.00000	0.90000	-0.10000
	1.00000	0.80000	-0.20000
	1.00000	0.92000	-0.08000
	4.60000	5.01000	0.41000
	1.00000	0.90000	-0.10000
	1.25000	1.25000	0.00
	0.75000	0.60000	-0.15000
	2.50000	2.40000	-0.10000
	2.25000	2.28000	0.03000
	1.25000	1.04000	-0.21000
	0.75000	0.60000	-0.15000
	1.60000	1.55000	-0.05000
	1.50000	1.54000	0.04000



TABLE 3.4.

METHYLMETHACRYLATE	Area 1	Area 2	Difference
	0.75000	0.75000	0.00
	4.50000	4.46000	-0.04000
	1.25000	1.25000	0.00
	0.75000	0.82000	0.07000
	1.25000	1.20000	-0.05000
	2.50000	2.40000	-0.10000
	2.00000	2.30000	0.30000
	4.25000	4.20000	-0.05000
	5.50000	5.12000	-0.38000
	2.25000	2.90000	0.65000
	1.20000	1.00000	-0.20000
	0.90000	0.90000	0.00
	0.91000	0.91000	0.00
	2.70000	2.70000	0.00
	2.50000	2.44000	-0.06000
	5.54000	5.50000	-0.04000
	1.00000	1.01000	0.01000
	3.00000	3.07000	0.07000
	3.75000	4.10000	0.35000
	1.00000	1.10000	0.10000
	3.00000	3.10000	0.10000
	0.90000	1.10000	0.20000
	0.90000	0.94000	0.04000

TABLE 3.5.

ETHYLACETATE	Area 1	Area 2	Difference
	1.75000	1.70000	-0.05000
	1.50000	1.70000	0.20000
	1.90000	1.94000	0.04000
	3.00000	3.10000	0.10000
	1.60000	1.70000	0.10000
	1.50000	1.60000	0.10000
	1.00000	1.00000	0.00
	1.60000	1.50000	-0.10000
	3.25000	3.50000	0.25000
	2.25000	2.35000	0.10000
	2.00000	2.05000	0.05000
	1.50000	1.60000	0.10000
	5.00000	5.00000	0.00
	3.75000	3.76000	0.01000
	1.75000	1.76000	0.01000

TABLE 3.6.

## ORTHODICHLOROBENZENE

Area 1	Area 2	Difference
3.00000	2.99000	-0.01000
1.50000	1.24000	-0.26000
0.80000	0.83000	0.03000
2.00000	1.94000	-0.06000
1.25000	1.13000	-0.12000
1.00000	0.98000	-0.02000
1.50000	1.50000	0.00
3.00000	3.09000	0.09000
3.75000	3.73000	-0.02000
3.25000	3.28000	0.03000
1.25000	1.17000	-0.08000
3.00000	2.66000	-0.34000
1.50000	1.50000	0.00
1.00000	0.99000	-0.01000
2.25000	2.10000	-0.15000
1.25000	1.21000	-0.04000

TABLE 3.7.

## BENZENETRICARBONYLCHROMIUM

Area 1	Area 2	Difference
1.50000	1.60000	0.10000
4.00000	4.01000	0.01000
1.00000	1.00000	0.00
0.50000	0.60000	0.10000

TABLE 3.7. (Cont.)

0.50000	0.70000	0.20000
1.00000	1.01000	0.01000
0.50000	0.55000	0.05000
1.00000	1.11000	0.11000
0.90000	0.89000	-0.01000
1.50000	1.52000	0.02000
1.00000	1.00000	0.00
2.00000	2.30000	0.30000
5.50000	5.61000	0.11000
4.30000	4.31000	0.01000
3.00000	2.91000	-0.09000
2.50000	2.55000	0.05000
1.00000	1.10000	0.10000
4.59000	5.03000	0.44000
1.00000	0.99000	-0.01000
2.00000	1.92000	-0.08000
1.00000	0.92000	-0.08000
5.55000	5.99000	0.44000
1.00000	1.02000	0.02000
1.50000	1.60000	0.10000
4.99000	5.10000	0.11000
1.50000	1.50000	0.00
3.40000	3.30000	-0.10000
2.59000	2.60000	0.01000
1.00000	0.99000	-0.01000
3.00000	2.99000	-0.01000
3.00000	3.10000	0.10000
4.50000	4.49000	-0.01000

TABLE 3.8.

## HEPTACOSAFLUOROTRIBUTYLAMINE

Area 1	Area 2	Difference
5.50000	5.46000	-0.04000
5.00000	4.40000	-0.60000
5.00000	4.49000	-0.51000
3.50000	3.00000	-0.50000
4.00000	3.88000	-0.12000
5.00000	4.31000	-0.69000
1.00000	1.32000	0.32000
6.00000	6.28000	0.28000
0.50000	0.30000	-0.20000
3.00000	2.65000	-0.35000

TABLE 3.9.

## ROTARY PUMP OIL OF THE MS9

Area 1	Area 2	Difference
4.50000	3.90000	-0.60000
1.50000	1.21000	-0.29000
5.00000	4.94000	-0.06000
1.00000	1.05000	0.05000
2.00000	2.08000	0.08000
4.50000	4.09000	-0.41000
3.50000	3.20000	-0.30000
1.00000	0.97000	-0.03000
1.59000	1.65000	0.06000
1.00000	0.99000	-0.01000

TABLE 3.10.

## BICYCLOHEPTATRIENYLHEXACARBONYLDICHRONIUM

Area 1	Area 2	Difference
2.50000	2.11000	-0.39000
1.00000	0.90000	-0.10000
0.50000	0.70000	0.20000
1.50000	1.50000	0.00
1.10000	1.14000	0.04000
3.00000	2.23000	-0.77000
3.00000	2.37000	-0.63000

TABLE 3.11.

## BACKGROUND SPECTRUM OF THE MS9

Area 1	Area 2	Difference
1.50000	1.40000	-0.10000
0.50000	0.60000	0.10000
1.00000	1.03000	0.03000

### 3.4. Discussion of Results

As has been mentioned earlier in this chapter, some authors have assumed the shape of the peak to be triangular and have used this assumption in their mathematical treatments without any further proof.

In the present work an attempt has been made to show by means of a mathematical treatment that the peak produced on the chart paper of the mass spectrometer can be accurately considered as having a triangular shape. This theoretical treatment has been supported by the experimental results obtained from measurement of peak areas by both the triangular formula and the planimeter.

Inspection of these results shows that the two methods of measuring the areas of the peaks yield the same information; the abundance measurements calculated from both sets of peak areas show insignificant standard deviation and mean error. However the triangular method of measuring the area is much more simple and rapid, and measurement of areas with a planimeter involves more risk of human error. Also, when there are double peaks in the spectrum as shown in figure 3.4, the outline of each peak is not well defined because they overlap and this makes the measurement of the area with the planimeter very difficult. The triangular method used in the present work does not involve the extremities of the peaks and is therefore much more suitable in such a case.

In most automatically performed abundance measurements, where data processing is carried out by a computer either on-line or off-line to the mass spectrometer, it is usual for the peak area, and not the peak height to be chosen as the variable representative of the information required.<sup>4, 7, 11, 12, 13.</sup> If the peak is taken as a triangle, the digitisation of data is much simpler than with any other peak shape (gaussian, sinusoidal, etc.).

An attempt has been made to prove that the peak is of triangular shape for slow scans in the present work. However, the peak can still be treated as a triangle in fast scans, as has been shown by Banner<sup>6</sup>. So, in both slow and fast scans, the assumption of triangular peak shape makes the task of measuring ion abundances simpler, quicker and more reliable than alternative treatments would allow.

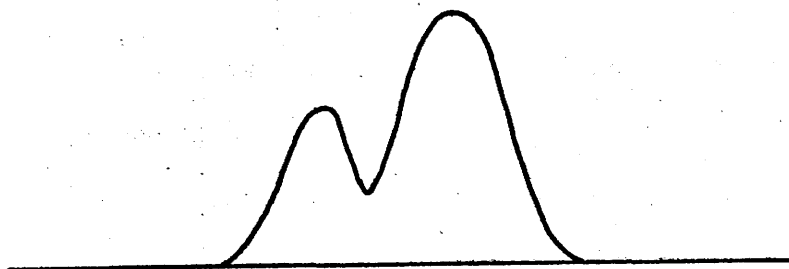


Fig. 3.4

... and G. H. ... The Mathematics  
 ... D. Van Nostrand Co., London, 1914,  
 ... and J. H. Holliday, 19th Ann. ...  
 ...  
 ... and J. L. ...  
 ... Smith and R. W. Olsen, Ar  
 ... 13.



Bibliography (Chapter 3).

1. F.W. Aston, Phil. Mag., 1919, 38, 707; *ibid.*, 709.
2. J.J. Thomson, Phil. Mag., 1911, 21, 225.
3. J.H. Beynon, "Mass Spectrometry and its Applications to Organic Chemistry," Elsevier Publishing Co., Amsterdam, 1960, p.60.
4. (a) W.J. McMurray, S.R. Lipsky and B.N. Green in "Advances in Mass Spectrometry," Vol.IV, Ed. E. Kendrick, The Institute of Petroleum, London, 1968, p.86.  
(b) A.L. Burlingame in Reference 4 (a) p.28.
5. A. Carrick, Int. J. Mass Spect. and Ion Phys., 1969, 2, 333.
6. A.E. Banner, J. Sci. Instr., 1966, 43, 138.
7. (a) H.C. Bowen, E. Clayton, D.J. Shields and H.M. Stanier in Reference 4, p.257.  
(b) R. Venkataraghavan, F.W. McLafferty and J.W. Amy, Analyt. Chem., 1967, 39, 178.  
(c) L.Fraser Monteiro and R.I. Reed, Int. J. Mass Spect., and Ion Phys., 1969, 2, 265.
8. Fowler, PhD Thesis, University of London, 1957.
9. R.C. Jennison, "Fourier Transforms and Convolutions for the Experimentalist," Pergamon Press, London, 1961, Chapters 5 and 6.
10. H. Margenau and G.H. Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand Co., London, 1964, Vol.I, Chapter 8.
11. A.J. Campbell and J.S. Halliday, 13th Ann. Conf. on Mass Spect., St. Louis, May, 1965, p.200.
12. B.N. Green, T.O. Merren and J.G. Murray in Reference 11, p.204.
13. A.L. Burlingame, D.H. Smith and R.W. Olsen, Analyt. Chem., 1968, 40, 13.

Chapter 4.The determination of ionisation potentials and  
bond dissociation energies of some organic compounds4.1. Introduction

Since the pioneering work by P. Lenard<sup>1</sup> on ionisation phenomena, followed by the first important quantitative investigations of J. Franck<sup>2</sup> and G. Hertz<sup>3</sup>, it has become clear that there are various critical energies which an impacting electron can transfer to an atom. Thus the Bohr theory was supported by critical potential experiments carried out with atoms. This study became more complicated with diatomic molecules owing to the complication of the dissociation resulting from the electron-impact.

Professor Tate<sup>4,5,6</sup>, his students, and D.P. Stevenson and J.A. Hipple<sup>7,8,9</sup> later used mass spectrometry as an important tool for the determination of the ionisation potentials and dissociation energies of organic molecules.

The interaction between the molecules of a gas and electrons of sufficient energy causes ionisation with or without dissociation leading to the formation of positive or negative ions. The formation of positive ions is more favoured than that of negative ions<sup>10</sup> and only the formation of positive ions under electron-impact will be considered here.

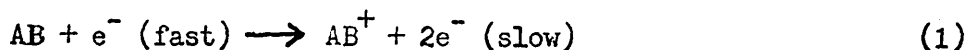
The probability that any molecule of a given species will be ionised by collision with an electron of a given velocity may be specified in terms of an ionisation cross-section. The number of ions produced is proportional to this ionisation cross-section of the gas, provided that the pressure is low enough to ensure that ion-molecule reactions do not take place<sup>11</sup>.

If a monatomic species is considered, the molecular ion is

produced, depending on the energy of the ionising particle, in its fundamental electronic state or in one of its excited electronic states. There is also the possibility of autoionisation; that is, a neutral atom appears in an excited electronic state above that of the appearance of the ion and this excitation is followed by a non-emission transition which takes the atom to an ionised state.

If the molecule is diatomic, in addition to the phenomena described above, the molecular ion will also possess vibrational energy.

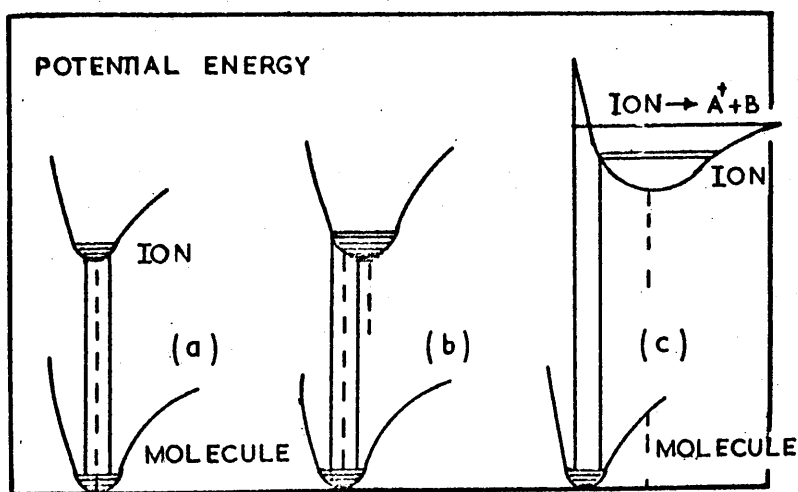
In general, the ionisation of a molecule AB which gives the molecular ion  $AB^+$  occurs in the following manner:



There is not, during the course of an electronic transition, any appreciable change in the configuration and momentum of the nuclei of the molecule. This is the essence of the Franck-Condon principle. An alternative statement of the principle is that the most probable transitions are to those states which lie vertically over the populated levels of the ground state.

Examining the potential energy curves of a diatomic molecule in its fundamental state and the corresponding ionised state, four possible cases can be distinguished and the first three are represented by the curves shown in Fig.4.1.

In the first case, the internuclear distances corresponding to the minima in the potential energy curves are the same in the ion and in the molecule and so the most probable transition occurs between the vibrational levels of quantum number  $v = 0$ . This transition corresponds to the adiabatic ionisation potential or first ionisation potential of a molecule, which is defined as the difference in energy between the ground vibrational level of the lowest electronic state of the molecule and the fundamental vibrational level of the molecular ion. It may be impossible to produce the molecular ion in its ground



INTERNUCLEAR DISTANCES

FIGURE 4.1.

... of kinetic energy.

... the separation of a molecule AB which gives a

... ion A<sup>+</sup> occurs as follows.

... reaction  $A^+ + B + \Delta e^-$  (slow) ... (2)

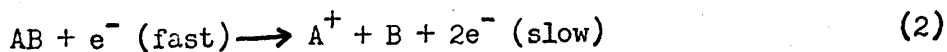
state by electron-impact and so the measured value of the minimum energy necessary to produce the molecular ion may not equal but exceed the adiabatic ionisation potential<sup>12</sup>. The adiabatic ionisation potential in such a case is determined by the convergence limit of an appropriate Rydberg spectroscopic series<sup>10</sup>.

In the second case, the internuclear distances corresponding to the minima in the potential energy curves are different in the cases of the molecule and the ion and so the most probable transition is from a level  $v = 0$  of the molecule to an excited vibrational level of the ion. In this case, the ionisation potential measured is described as vertical and is defined as the minimum energy necessary to remove an electron from a molecule without change in the nuclear configuration. This potential is greater than the adiabatic ionisation potential and only approaches the latter as the internuclear distances corresponding to the minima in the potential energy curves of the neutral molecule and the ion approach each other.

In the third case, the potential energy curve of the ion can be such that the most probable transitions lie above or near the level corresponding to the dissociation. In this case, most transitions give rise to dissociation and the abundance of molecular ions is very small.

In the fourth case (not illustrated) the transition occurs to an unstable ionic state. In this case, the excited state always lies in the continuum; fragmentation accompanies all such transitions, with varying amounts of kinetic energy.

In general, the ionisation of a molecule AB which gives a fragment ion  $A^+$  occurs as follows.



For this fragment ion, an appearance potential can be defined as that minimum energy necessary to form the fragment in its ground state from

the molecule in its ground state.

In practice, both the molecule and the molecular ion may be in excited states and therefore there can be a difference between the determined ionisation or appearance potentials and the theoretical values<sup>13</sup>.

A relationship such as equation (3) is useful in the interpretation of these phenomena.

$$AP(A^+) = D(A - B) + IP(A) + E + K, \quad (3)$$

where  $AP(A^+)$  is the appearance potential of the ion  $A^+$ ,  $D(A - B)$  is the bond dissociation energy of the molecule  $AB$ ,  $IP(A)$  is the ionisation potential of the radical  $A$ ,  $K$  and  $E$  are respectively the kinetic energy and the excitation energy of the dissociation products. The excitation energy includes electronic, vibrational and rotational components.

In the case of polyatomic molecules, the potential energy curves are replaced by multidimensional potential energy surfaces and the study of these becomes much more complicated<sup>14</sup>.

The determination of ionisation and appearance potentials by the electron-impact method is carried out in two stages. Firstly, an ionisation efficiency curve is obtained for the ion under study; secondly, the interpretation of this curve has to be undertaken.

When the number of positive ions (or ion current) produced in an experiment is determined as a function of the electron energy, an ionisation efficiency curve is obtained. Many investigators have studied the shape of the ionisation efficiency curves for certain ion species in the vicinity of the ionisation potential. The initial portion of a typical ionisation efficiency curve for a monatomic gas is shown in Fig.4.2. According to Honig<sup>15</sup>, the section designated 'a' is exponential in character, section 'b' is intermediate and section 'c' is essentially linear for energies exceeding the ionisation

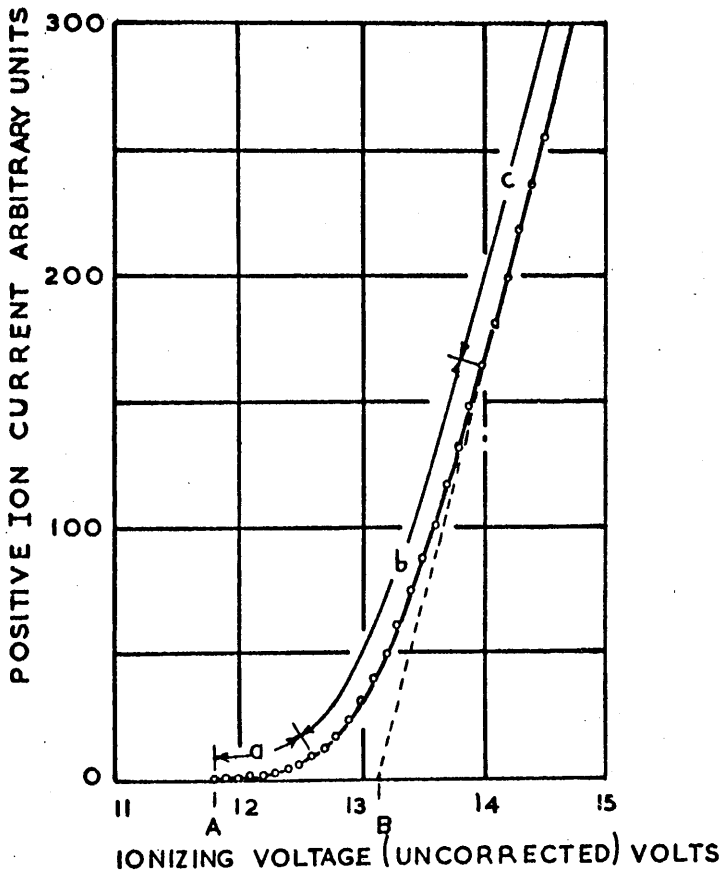


FIGURE 4.2.

potential by about 1 eV. Such curves usually reach a maximum at 20 to 50 eV above the ionisation threshold and then gradually decay with any further increase in electron energy. In chemical analysis, the electron energies used are usually in the region 50-100 eV because the maximum efficiency of ionisation lies in this range<sup>6</sup>.

There have been several theoretical studies intended to predict the shape of the curve immediately above the threshold energy of ionisation.

Geltman<sup>16</sup> has predicted theoretically that a linear law should apply for single ionisation while Wannier<sup>17</sup> has presented an argument in favour of a much more complex law. This law involves the 1.127th power of the excess energy above the ionisation threshold for single ionisation and a near  $n$ th power,  $n$  being an integer, for multiple ionisation. Other authors<sup>18,19,20</sup> have also studied the probabilities of single and multiple ionisation processes but at present there is no exact treatment available.

Since electrons are generally obtained by heating a filament at high temperatures, the beam is energetically heterogeneous. Under such conditions the emission obeys Richardson's law and the emitted electrons show a more or less wide energy distribution which is Maxwellian in character<sup>15,21</sup>. Most of the curvature observed in the ionisation efficiency curve near the onset of ionisation arises from this cause. The effect of this spread in energies upon the curve shape has been studied in detail<sup>7,15,22</sup> and methods of eliminating this difficulty have been devised.

There are several sources of error which can significantly reduce the accuracy of measurement of ionisation potentials by mass spectrometry<sup>23</sup>. Those most deserving of mention are the existence of a potential gradient within the ionisation chamber, the increase in the temperature of the filament which increases the spread of electron



energies, and the variation of contact potentials within the ionisation chamber. A second compound is usually introduced as a standard when measuring an ionisation potential in order to eliminate the source of error due to the variation of contact potentials.

A variety of methods are used for the determination of the ionisation potential from the ionisation efficiency curve. All have some disadvantages and all attempt to eliminate as far as possible the uncertainties introduced by the heterogeneity of the electron beam. The majority of these techniques make use of a standard compound, the ionisation curve of which is compared with that of the compound for which the ionisation potential is to be calculated. The standard compound is usually a noble gas having a spectroscopically established ionisation potential and is introduced simultaneously with the other compound. Practical considerations dictate that whenever possible the ionisation potential of the standard gas should be very close to that of the compound to be determined. The partial pressures of the two substances are adjusted to give ion beams of comparable magnitudes. Among the techniques most used are the following:

- 1) Linear extrapolation technique proposed by Smith<sup>24</sup>.

The linear portions of the ionisation curves of the standard and the test compound are extrapolated to zero current. The difference between these extrapolated values is taken to be the difference between the two ionisation potentials. This method only provides an upper limit of ionisation potential in most cases and is not now widely used.

- 2) Initial break or vanishing current technique.

In this technique<sup>25</sup> the ionisation efficiency curve is extrapolated back to its intersection with the energy axis, this point being a measure of the ionisation potential. However, because of the effect of the electron energy spread, the curve tends to be asymptotic to the energy axis and there is usually no sharp break. In addition,

the position of the point located in this way is dependent on sample pressure, the number of bombarding electrons and the sensitivity of the amplifier. The situation improves somewhat when the standard compound is introduced.

3) The extrapolated difference technique of Warren<sup>26</sup>.

This is an improved version of the vanishing current technique. In this case the scales of the ordinates of the ionisation efficiency curves of both the compound and the standard are adjusted so that the linear parts are parallel. The differences in voltage between the curves are then plotted as a function of ion current. The line thus obtained is extrapolated to zero current and the voltage corresponding to that point is taken as the difference between the ionisation potentials of the two gases. This method usually gives good results.

4) Logarithmic methods.

The oldest of these methods, the critical slope method, was proposed by Honig<sup>15</sup>. This takes into account the energy spread of the electrons. A semilog plot of the ionisation efficiency curve will give a curve with a slope of  $\frac{2}{3kT}$  at the ionisation potential,  $k$  being the Boltzmann constant and  $T$  the absolute temperature of the filament. This method enabled Honig to obtain good experimental values for the ionisation potentials of hydrocarbons.

An adaptation of Honig's technique has been made by Lossing<sup>27</sup>. It usually gives good and reproducible results, especially when the shapes of the curves to be compared are not too different. After adjusting the pressure to yield comparable ion intensities at 50 eV, a log plot of peak heights, as percentages of the abundance at 50 eV, against the electron energy yields parallel curves near the onset of ionisation. Generally, voltage differences <sup>of</sup> ~~at~~ 1% of the intensity at 50 eV are taken as significant.

The semilogarithmic method has been favoured by experimentalists as it is quite easy to use and gives good results.

More recently, other interesting methods have been proposed, always with the aim of eliminating the effect of energy spread. Thus the derivative method of Morrison<sup>28</sup>, based on the determination of differential curves from the ionisation efficiency curves, permits the study of the fine structure of the ionisation curves and provides information on the excited states of the ions.

Alternatively, the deconvolution method, also by Morrison<sup>29</sup>, is based on the use of Fourier transforms and computerised noise removal; many structural details can be elucidated from the curves.

Other workers have tried to avoid the energy spread of the bombarding electrons by developing techniques and constructing apparatus for the specific purpose of producing a monochromatic electron beam. Two different approaches to this problem have been made.

One is based on the use of an electron spectrometer in which deflection of electrons in a magnetic or electrostatic field is used as a way of selecting a beam of narrow energy spread.

In the early work of Nottingham<sup>21</sup> a magnetic selection method was used, but more recently Clarke<sup>30</sup> has built an electrostatic velocity selector. With this apparatus he was able to observe segmented straight lines with little curvature as the ionisation potential was approached. The technique has been further improved by Marnet and Kerwin<sup>31</sup>.

The other approach to the problem was made by Fox and coworkers<sup>32</sup> with the "Retarding Potential Difference" method. It is based on the use of a special electron gun with at least two supplementary electrodes, the design being such that the energy of the electrons is confined to a small range and ion formation takes place in a field-free region. Using this technique, the ionisation potentials

obtained are closer to those calculated by spectroscopic methods than results obtained from techniques employing heterogeneous electron energies. Recently this method has been improved<sup>33</sup> to give ionisation potentials which agree to within  $\pm 0.02$  eV of the spectroscopic values.

Theoretical calculations of ionisation potentials are very complex for diatomic and polyatomic molecules, though manageable for some monatomic species. There are several methods, including the equivalent orbital method and the group orbital method<sup>34</sup>. Often there is agreement between results calculated by these methods and the experimental ones.

Bond dissociation energies and heats of formation can be deduced from ionisation and appearance potentials in conjunction with calorimetric data<sup>35</sup>.

The minimum energy necessary for the appearance of an ion can be considered as equal to the change in enthalpy which occurs in the reaction concerned, provided that no excess energy is involved.

If the molecule AB gives fragmentation to  $A^+$  in the following way:



the appearance potential of  $A^+$  can be expressed as follows:

$$\Delta H^{\circ} = AP(A^+) = \Delta H_f^{\circ}(A^+) + \Delta H_f^{\circ}(B) - \Delta H_f^{\circ}(AB) \quad (5)$$

$\Delta H^{\circ}$  being the heat of the reaction in which the fragment ion is formed and  $\Delta H_f^{\circ}$  the heats of formation of the species indicated.

The heat of formation of the ion  $A^+$  can be calculated provided that the heats of formation of the other fragments and of the molecule are known. The heat of formation of the electron is taken as zero at all temperatures<sup>36</sup>. In criticism of these calculations it has been pointed out that the temperature at which the measurements of appearance potentials are made is not known, but as this effect is not important it is assumed that the conditions are those of an ideal gas at 25°C<sup>36</sup>.

The heats of formation can also be calculated by a group theory method<sup>37</sup>, if not known experimentally. The importance of the information provided by heats of formation of positive ions in the study of molecular structure is discussed by Wacks and coworkers<sup>38</sup>.

Alternatively,

$$IP(A) = \Delta H_f^{\circ}(A^+) - \Delta H_f^{\circ}(A) . \quad (6)$$

Combining this expression with expressions (3) and (5), and supposing  $K + E = 0$ , the following expression is obtained:

$$D(A - B) = \Delta H_f^{\circ}(A) + \Delta H_f^{\circ}(B) - \Delta H_f^{\circ}(AB) . \quad (7)$$

Hence the bond dissociation energy may be derived in an indirect way from electron-impact data in conjunction with available thermochemical data.

From expression (3), if the ionisation potential of the radical and the appearance potential of the fragment ion are known, bond dissociation energy can be directly calculated.

Bond dissociation energy in positive ions can also be calculated by mass spectrometry<sup>10</sup>. For an ion  $AB^+$  the upper limit of the bond dissociation energy will be given by

$$D_1(A - B)^+ \leq AP(A^+) - IP(AB) \quad (8)$$

and

$$D_2(A - B)^+ \leq AP(B^+) - IP(AB) \quad (9)$$

for the two possible processes of fission, but by Stevenson's rule<sup>39</sup> usually only the less energetic mode of fragmentation occurs as the charge will tend to be localised on the fragment with lower ionisation potential.

The determination of ionisation and appearance potentials of free radicals is most important in the calculation of bond dissociation energies. Most of the techniques used are based on the initial work of Eltenton<sup>40</sup> and Hipple and Stevenson<sup>41</sup>. Since these studies, the most important contribution to the development of this subject has been made by Lossing and Tickner<sup>42</sup>.

If the kinetic energy involved in expression (3) is not negligible, it has to be calculated. Hagstrum<sup>43</sup> developed a method for the determination of kinetic energies of fragment ions in a specially designed instrument based on the application of retarding potentials to ion-discriminating plates. Other methods, to determine excess kinetic energy, include deflection techniques<sup>44</sup> and the study of peak shapes<sup>45</sup>. However, very often fragment ions are formed without excess energy.

While having a theoretical application in the determination of excited energy levels, bond dissociation energies, heats of formation and molecular structures, the ionisation and appearance potentials have other practical applications. An example is the differentiation between isomers, one of which would have a lower ionisation potential. This has been suggested<sup>46</sup> for the differentiation of  $\alpha$ - and  $\beta$ -glycosidic linkages in carbohydrates, where the former was found to give a lower value.

Several authors have studied the variation of the ionisation potential with the structure of the molecules. Honig<sup>15</sup> carried out such a study for alkanes, alkenes and alkynes, in which he noted the decrease of ionisation potential with increase in chain size. Similarly, results have been obtained for hydrocarbon radicals and halogenated methyl radicals<sup>47</sup>. A more general study of this variation of ionisation potentials has been based on concepts such as conjugation, induction and electronegativity<sup>48</sup>. More recently, this type of work has been carried out<sup>49</sup> with metallocenes and related complexes, in which the ionisation potentials of the substituted metallocenes are related to the ionisation potential of the substituent, the C-O stretching frequency, the  $\nu(\text{CO})$  force constant and the Hammett sigma values of the substituents. Also, in this work, equations were formulated to permit calculation of ionisation potentials of complexes from the ionisation

potential of a single complex and other additional values. Electron-impact studies have also led to the discovery of excited states of aromatic hydrocarbons such as benzene, naphthalene, anthracene and phenanthrene<sup>50, 51</sup>.

In the past few years the number of papers concerned with these studies has increased considerably.

Ionisation and appearance potentials and heats of formation of most gaseous ions have been compiled<sup>36</sup>.

A theory of ionisation potentials in which allowance is made for the effect of long-range dipolar potentials inside the molecule has been presented<sup>52</sup>; Hartree-Fock calculations have also been applied to ionisation potentials<sup>53</sup>.

Electron-impact measurements of ionisation potentials can now be made with considerable precision. Lossing<sup>54</sup> has reported appearance potentials measured with an energy-selected monoenergetic electron beam from which he has established the existence of the cyclopropenyl ion  $C_3H_3^+$ .

Refinement in the measurement of ionisation potentials can be made by mathematical methods, without energy analysis of the electron beam. A computer method has been devised by Johnstone and coworkers<sup>55</sup>. This is called the ionisation efficiency/energy distribution difference (IE/EDD) method, and values of an accuracy comparable to that of photoionisation are claimed.

The advantages of deconvoluting ionisation efficiency curves have been pointed out<sup>56</sup> and it has been suggested that a third-derivative<sup>57</sup> method for determining ionisation potentials is superior to the procedure of Morrison<sup>28</sup>.

The use of appearance potential measurements for the determination of ion structure has been extensively discussed by several authors<sup>58</sup>.

In this work, a critical comparison has been made of literature values of ionisation and appearance potentials for methanol and its fragments with the same quantities as calculated by the electron-impact method. Similar measurements were made for deuterated methanol and ethylene glycol. The bond dissociation energies of methanol, deuterated methanol and ethylene glycol were also determined.



#### 4.2. Experimental and Results.

All compounds used in this work were commercially available samples of as high initial purity as possible. The deuterated methanol supplied by Prochem\*, was of 99.99% purity and was used as supplied; the other compounds, ethylene glycol and methanol, were subjected to further purification.

The methanol was purified<sup>59</sup> as follows. Most of the water was removed by fractional distillation; the methanol was then passed through a Linde type 4A molecular sieve and distilled again. Following treatment with sodium and a further distillation, the water content was about  $5 \times 10^{-5}\%$ <sup>60</sup>.

The ethylene glycol was dried<sup>59</sup> with anhydrous calcium sulphate and distilled under vacuum. It was further dried by reaction with sodium under nitrogen, refluxed for several hours and distilled. The distillate was then passed through a column of Linde type 4A molecular sieve and was finally distilled under nitrogen from a further portion of molecular sieve.

The argon gas used as reference compound was supplied by Air Products\*\*. The degree of purity was better than 99.9996%, the main impurities being:

O<sub>2</sub> ———< 1 vpm

H<sub>2</sub>O ———< 2 vpm

N<sub>2</sub> ———< 1 vpm

\* Prochem (British Oxygen Co. Ltd.),

Deer Park Road,

London, SW193UF,

U.K.

\*\* Air Products Ltd.,

Langmuir Road,

Bargeddie,

Baillieston,

Lanarkshire, G697TS,

U.K.

All measurements for the determination of ionisation and appearance potentials were carried out in an Associated Electrical Industries Ltd. (AEI) mass spectrometer, the single-focusing Nier geometry MS12, operating under the following conditions: resolving power 800, trap current 100  $\mu\text{A}$ , ion accelerating voltage 8 KV, ion source temperature  $120^{\circ}\text{C}$ , pressure in the source region  $4.8 \times 10^{-6}$  torr (1), bandwidth  $500 \text{ cs}^{-1}$ , scan speed 1.1 minutes per decade and chart speed  $2.54 \text{ cms}^{-1}$ . The ion repeller electrode was switched to zero, giving it the same potential as the cage, in order to make the ionisation chamber as field-free a space as possible. To facilitate the work, an AEI Mass Marker was coupled to the MS12.

The calibration compound, argon, was introduced through the cold inlet system and the compound under study was introduced simultaneously through the all-glass heated inlet system. The amounts of the two compounds introduced were regulated by adjusting the pressures to give approximately the same peak heights at 50 eV. During this adjustment, the pressure of the liquid was kept constant and the pressure of the argon was adjusted. In each experiment the electron energy was decreased from 20 eV in 0.4 eV steps until the heights of the two peaks concerned were negligible. The spectra were recorded using a Honeywell ultra-violet galvanometer recorder, with paper chart output. The heights of the peaks on the paper chart were measured for each electron voltage and the abundances of the ions were calculated as a percentage of the abundances at 50 eV. Then the log (peak-height) versus electron energy plots were drawn for each experiment. The curves for the compound under study and for the calibration compound were nearly parallel in all experiments over the region studied. These

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(1)  $1 \text{ torr} = 1.333 \times 10^2 \text{ Nm}^{-2}$  (S.I. Units).

curves are shown in Figures 4.3 - 4.8. The appearance and ionisation potentials were calculated by the Lossing method, as described previously, using the spectroscopic value of the ionisation potential for argon as 15.759 eV. The calculated values of the ionisation and appearance potentials of the ions under study are shown in table 4.1. In this table, the literature values found for these ionisation and appearance potentials are shown, together with the bond dissociation energies evaluated.

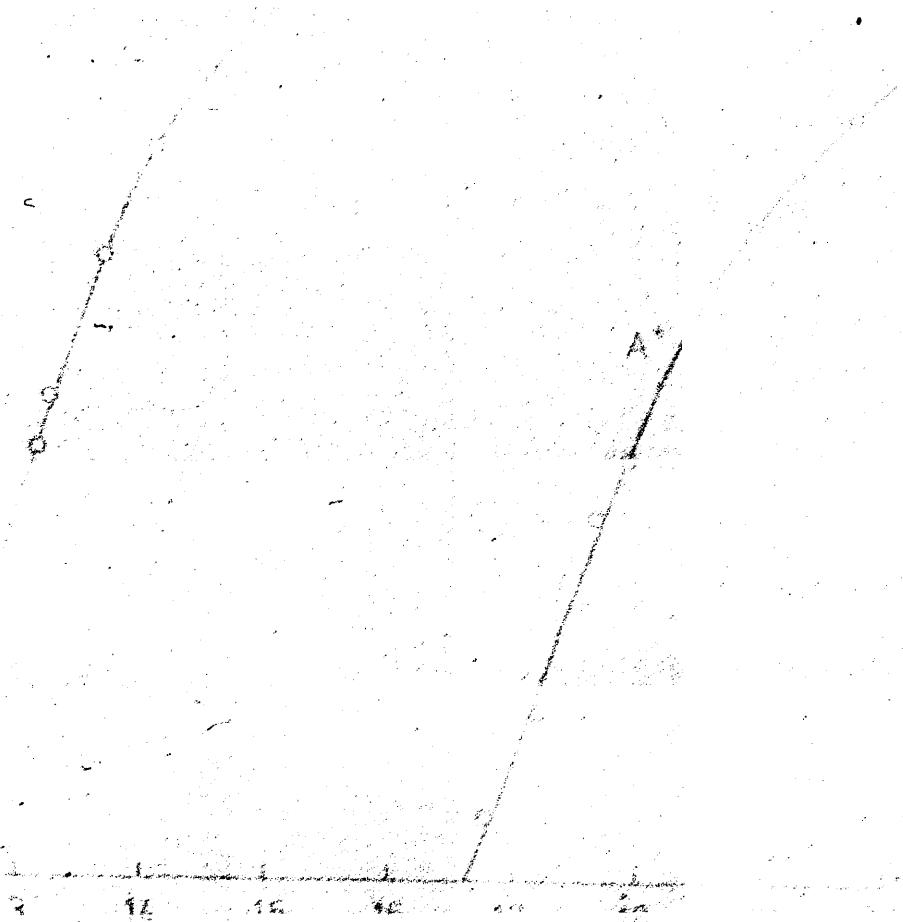


Figure 4.3

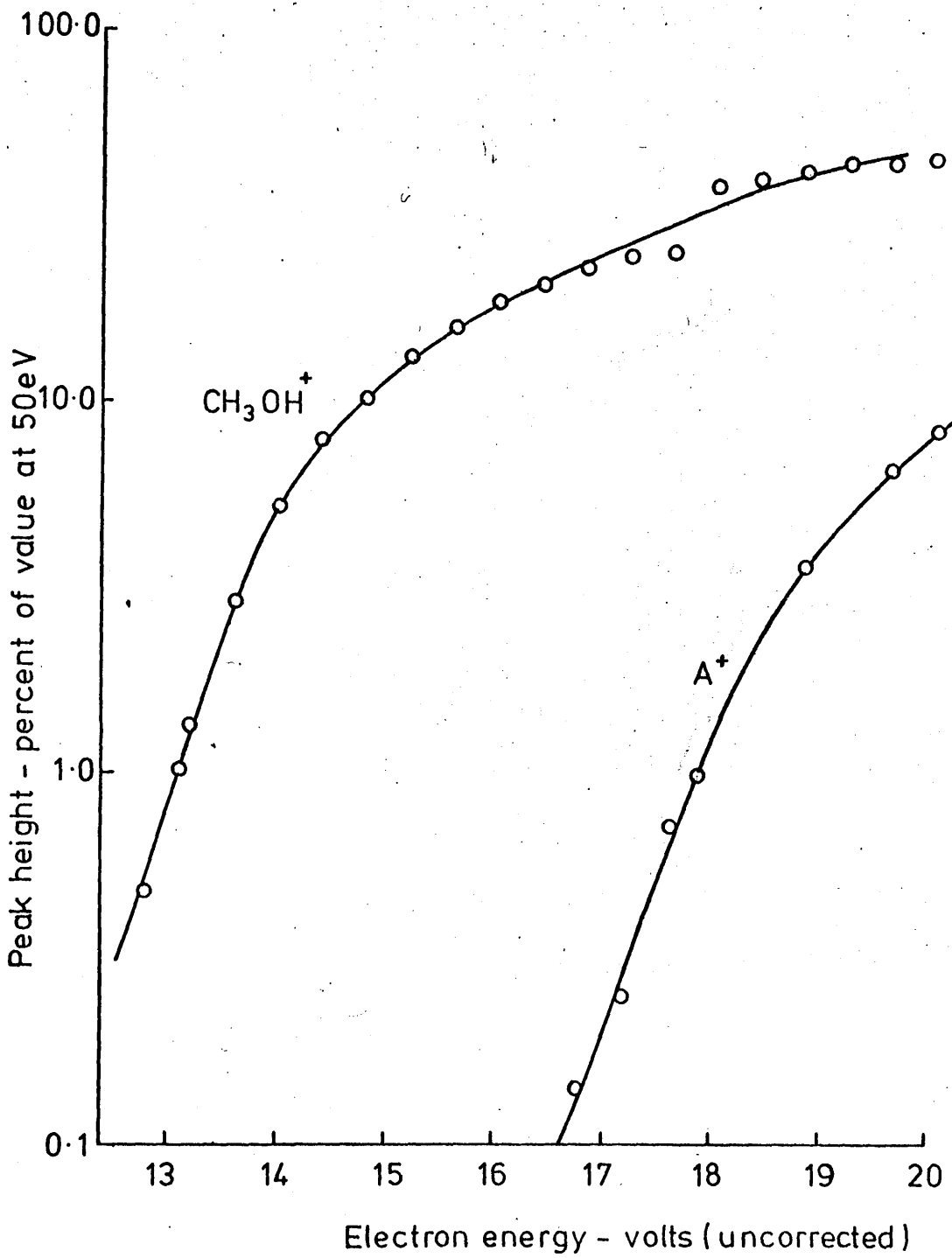


Figure 4.3.

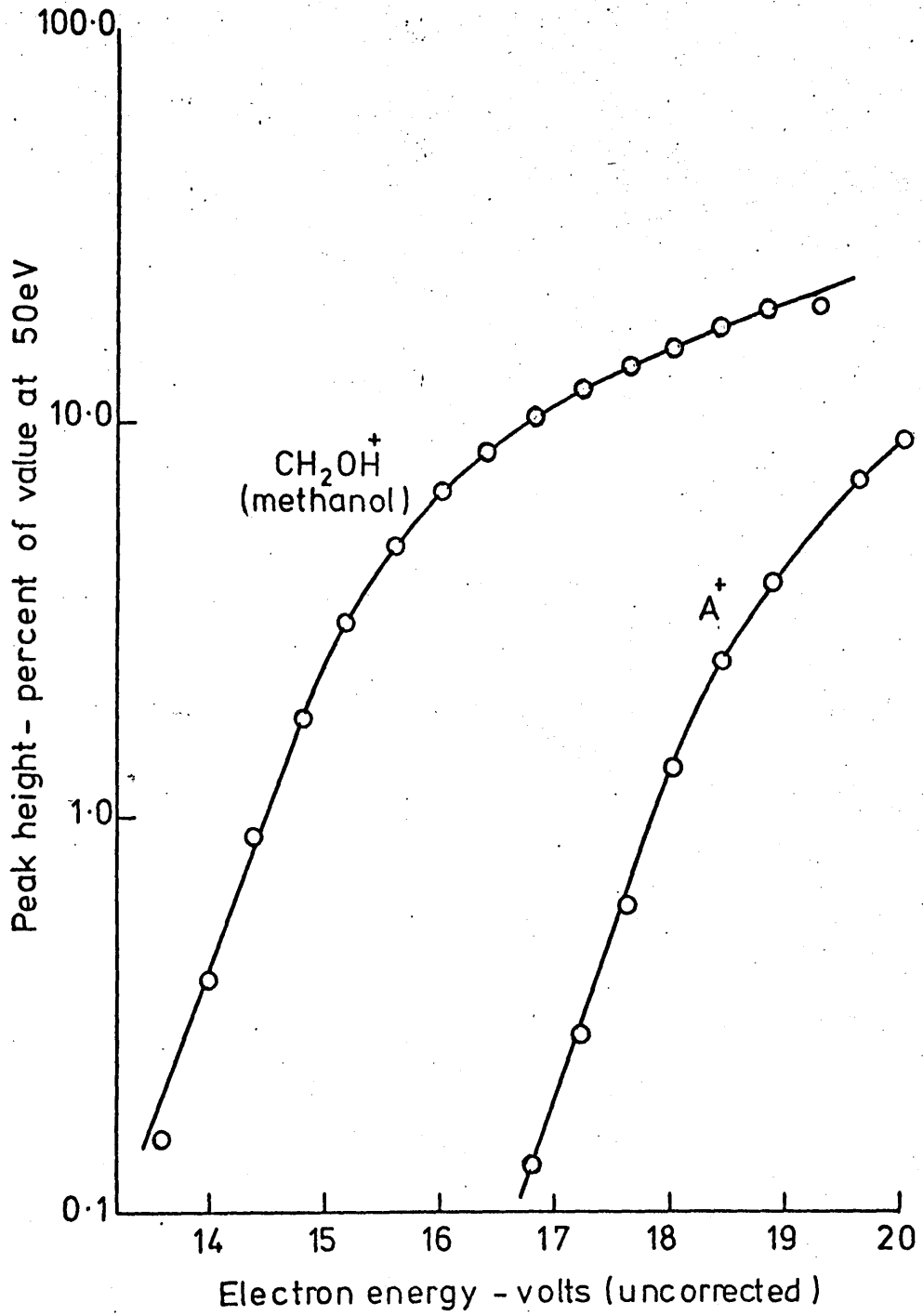


Figure 4.4.

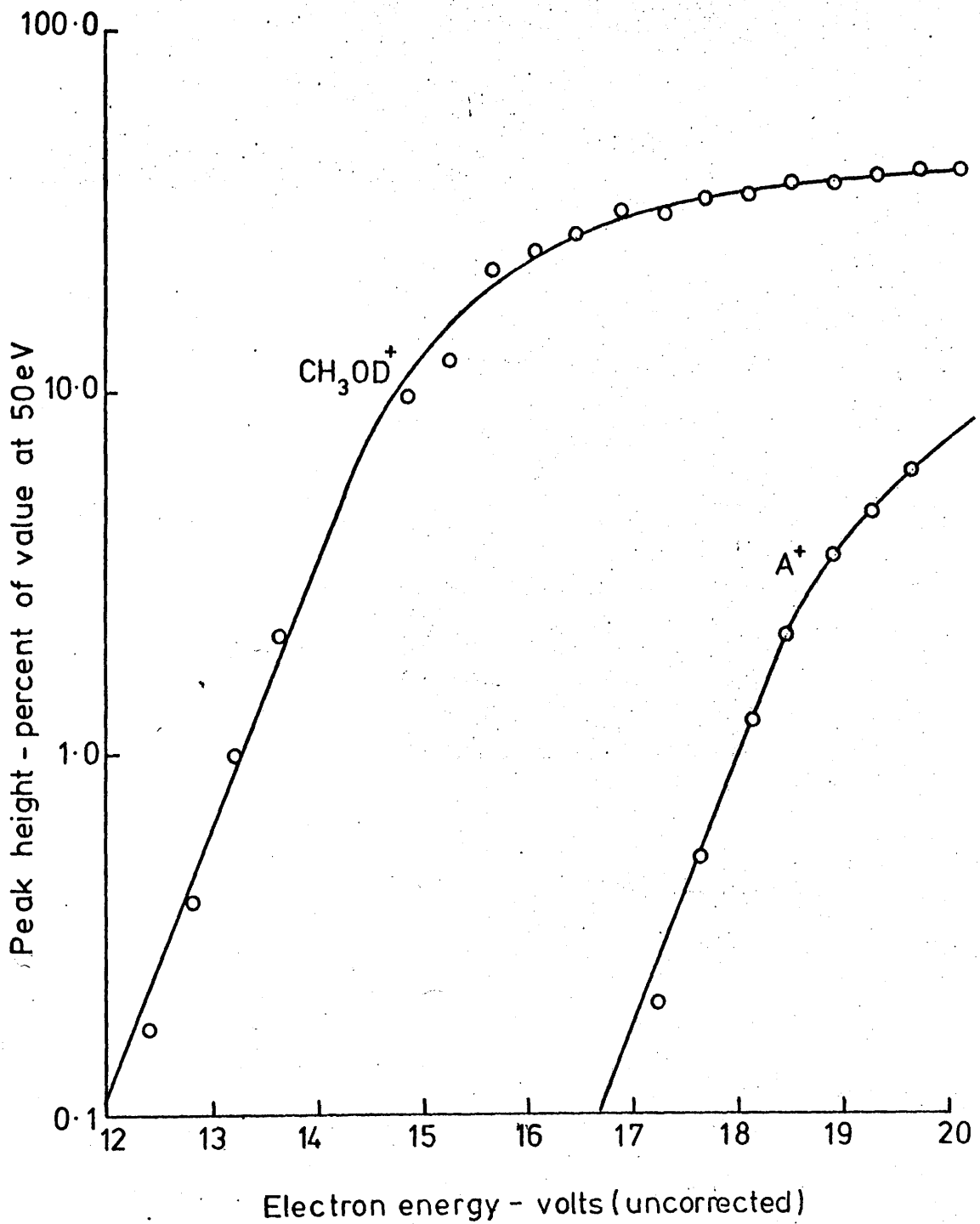


Figure 4.5.

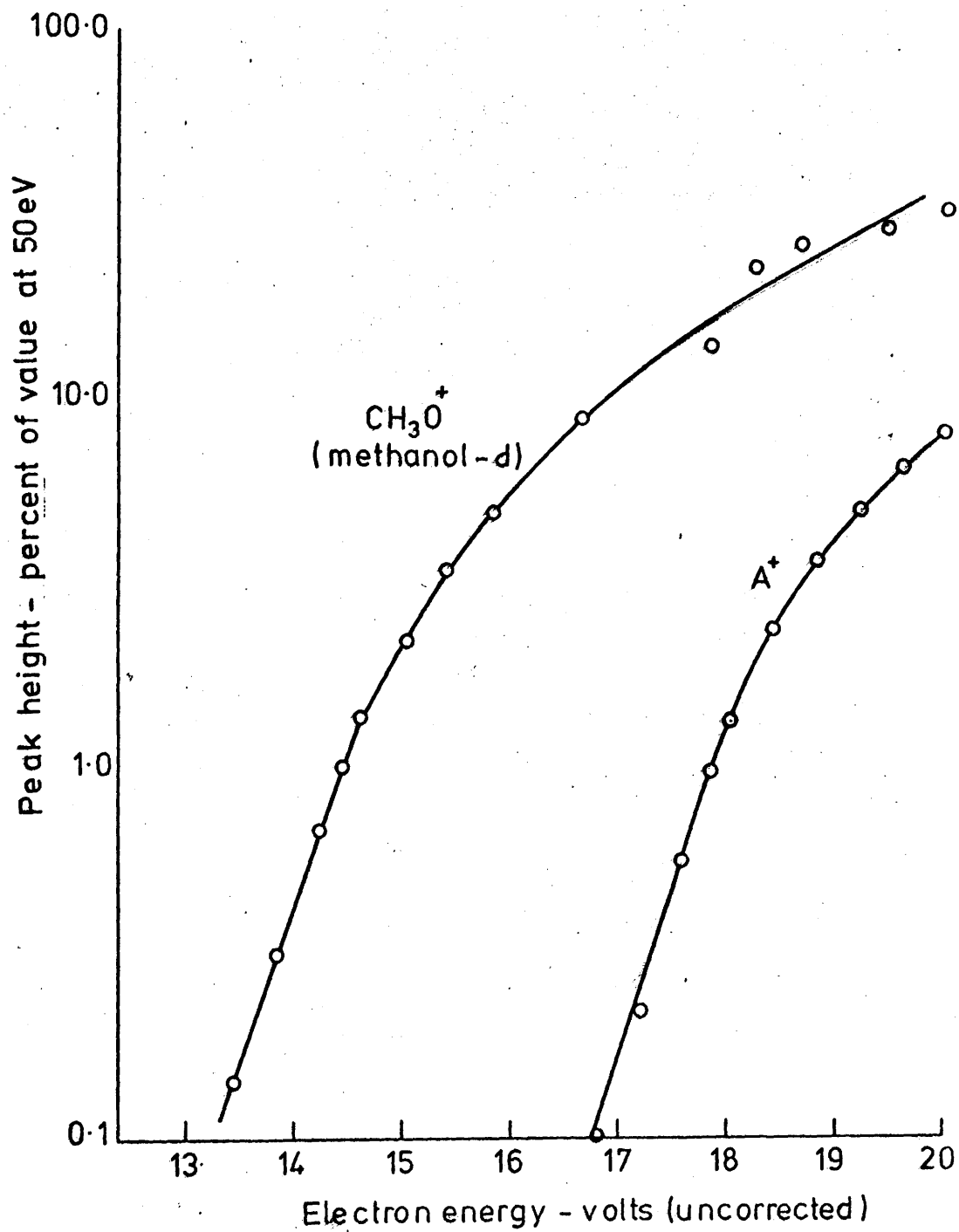


Figure 4.6.

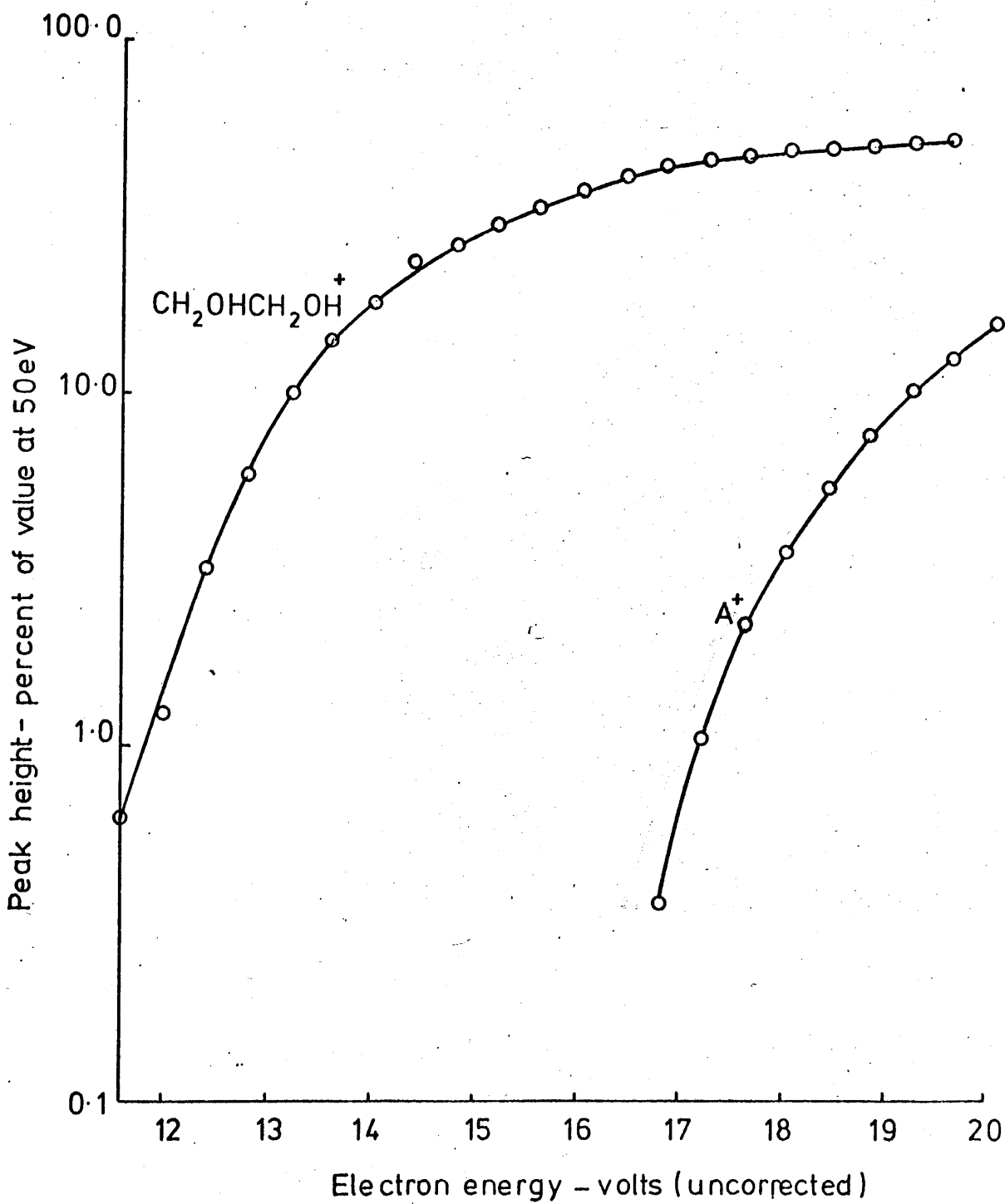


Figure 4.7.



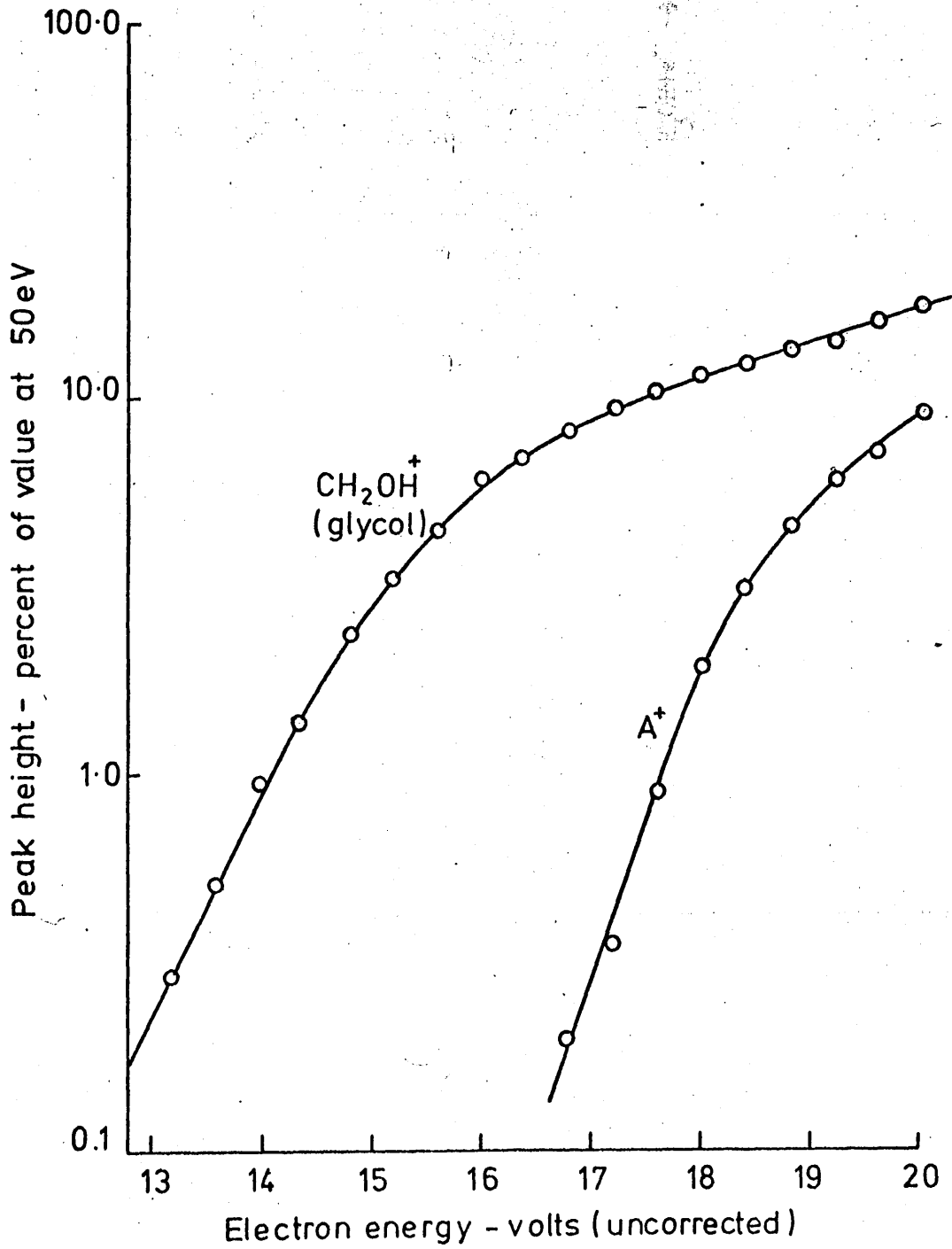


Figure 4. 8.

TABLE 4.1.

Ion or Radical	Ionisation and Appearance potentials obtained using the electron-impact method(eV)	Literature values (eV) * Method	Thermodynamic data (Kcal/mol <sup>-1</sup> )	Mechanism of the process
CH <sub>3</sub> OH <sup>+</sup>	11.01 ± 0.05	10.85 <sup>±</sup> -0.02 PI	ΔH <sup>o</sup> <sub>f</sub> (CH <sub>3</sub> OH <sup>+</sup> ) = 205.94	CH <sub>3</sub> OH+e <sup>-</sup> → CH <sub>3</sub> OH <sup>+</sup> + 2e <sup>-</sup>
		10.83 PE	ΔH <sup>o</sup> <sub>f</sub> (CH <sub>3</sub> OH) = -47.96	
		11.15 RPD		
		10.97 <sup>±</sup> -0.05 CS		
		10.9 IE		
		10.79 TC		
CH <sub>3</sub> O <sup>+</sup>	12.46 ± 0.05	12.32 RPD	ΔH <sup>o</sup> <sub>f</sub> (CH <sub>3</sub> O <sup>+</sup> ) = 184	CH <sub>3</sub> OH+e <sup>-</sup> → CH <sub>2</sub> OH <sup>+</sup> + H + 2e <sup>-</sup>
		12.1 <sup>±</sup> -0.1 VC	ΔH <sup>o</sup> <sub>f</sub> (CH <sub>3</sub> O) = -0.5	
		12.15 IE	D(CH <sub>3</sub> O-H) ≤ 102.85	
			D(CH <sub>3</sub> O-H <sup>+</sup> ) ≤ 33.44	
			D(CH <sub>3</sub> -OH) ≤ 89.02	

TABLE 4.1. (Contd.)

Ion or Radical	Ionisation and Appearance potentials obtained using the electron-impact method(eV)	Literature values (eV)	Thermodynamic data (Kcalmol <sup>-1</sup> )	Mechanism of the process
CH <sub>3</sub> O <sup>•</sup>	8.00			CH <sub>3</sub> O <sup>•</sup> +e <sup>-</sup> → CH <sub>3</sub> O <sup>•+</sup> + 2e <sup>-</sup>
CH <sub>3</sub> OD <sup>+</sup>	11.11 ± 0.05		D(CH <sub>3</sub> O-D) ≤ 108.62	CH <sub>3</sub> OD+e <sup>-</sup> → CH <sub>3</sub> OD <sup>+</sup> + 2e <sup>-</sup>
CH <sub>3</sub> O <sup>+</sup>	12.71 ± 0.05			CH <sub>3</sub> OD+e <sup>-</sup> → CH <sub>3</sub> O <sup>+</sup> +D+ 2e <sup>-</sup>
CH <sub>2</sub> OHCH <sub>2</sub> OH <sup>+</sup>	10.01 ± 0.05		ΔH <sup>o</sup> <sub>f</sub> (CH <sub>2</sub> OHCH <sub>2</sub> OH) ≥ -99.24	(CH <sub>2</sub> OH) <sub>2</sub> +e <sup>-</sup> → (CH <sub>2</sub> OH) <sub>2</sub> <sup>+</sup> + 2e <sup>-</sup>
CH <sub>2</sub> OH <sup>+</sup>	12.26 ± 0.05		D(CH <sub>2</sub> OH-CH <sub>2</sub> OH) ≤ 98.24 D(CH <sub>2</sub> OH-CH <sub>2</sub> OH <sup>+</sup> ) ≤ 51.89	(CH <sub>2</sub> OH) <sub>2</sub> +e <sup>-</sup> → CH <sub>2</sub> OH <sup>+</sup> +CH <sub>2</sub> OH+2e <sup>-</sup>

\* The method of measurement is indicated in an abbreviated form. Below are listed the abbreviations and their meanings.

Abbreviation	Method
PI	Photoionisation
PE	Photoelectron spectroscopy
RPD	Retarding potential difference
CS	Critical slope
LE	Linear extrapolation
TC	Theoretical calculation
VC	Vanishing current.

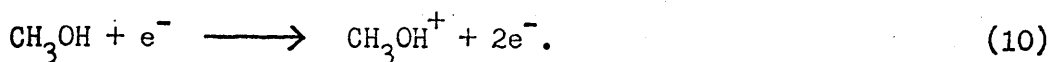
### 4.3. Discussion of Results.

The calculated values of the ionisation potential of  $\text{CH}_3\text{OH}$  and the appearance potential of  $\text{CH}_3\text{O}^+$  are in good agreement with the literature values, as can be seen by reference to table 4.1.

In none of the ionisation efficiency curves studied were excited states detected.

Using the values of the ionisation and appearance potentials calculated in the present work, several thermodynamic quantities were evaluated.

Assuming that there is no excess energy involved in the process of formation of  $\text{CH}_3\text{OH}^+$ , the energy of the threshold observed is the heat of reaction,  $\Delta H^\circ$ , for the process



That is,  $\Delta H^\circ = 11.01 \text{ eV} (253.90) \text{ Kcalmol}^{-1}$ \*

Taking as the heat of formation of  $\text{CH}_3\text{OH}^{**}$ , the value  $\Delta H_f^\circ(\text{CH}_3\text{OH}) = -47.96 \text{ kcalmol}^{-1}$ , the heat of formation of the ion  $\text{CH}_3\text{OH}^+$  may be calculated using the expression:

$$\Delta H_f^\circ(\text{CH}_3\text{OH}^+) = \Delta H_f^\circ(\text{CH}_3\text{OH}) + \text{IP}(\text{CH}_3\text{OH}). \quad (11)$$

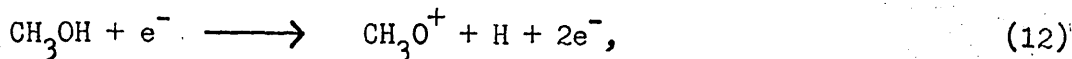
This gives  $\Delta H_f^\circ(\text{CH}_3\text{OH}^+) = 205.94 \text{ kcalmol}^{-1}$  which is in agreement, within the limits of experimental error, with the value of  $202 \text{ kcalmol}^{-1}$  based on the calculations of Watanabe<sup>61</sup>. If the mechanism

\* The conversion factor used was:  $1\text{eV} = 96487.0 \text{ J} = 23060.9 \text{ cal}$ .

\*\* The heats of formation  $\Delta H_f^\circ$  involved are taken at a standard state of  $25^\circ\text{C}$  and  $1 \text{ atm}$ , in  $\text{kcalmol}^{-1}$  units, with the heat of formation of the electron being taken as zero at all temperatures.

Except where otherwise indicated, all the values of heats of formation, ionisation potentials and appearance potentials are taken from Reference 36.

of formation of the ion  $\text{CH}_3\text{O}^+$  is:



it follows then,

$$D(\text{CH}_3\text{O} - \text{H}) \leq \text{AP}(\text{CH}_3\text{O}^+)_{\text{CH}_3\text{OH}} - \text{IP}(\text{CH}_3\text{OH}) \quad (13)$$

This bond dissociation energy would be an upper limit if excess energy is involved. The appearance potential of  $\text{CH}_3\text{O}^+$  is very close to the value found in the literature<sup>36</sup>, using the retarding potential difference method, which is usually in very good agreement with the spectroscopic value. Therefore, in this case it is assumed that no excess energy is involved in the process.

As the ionisation potential of the radical  $\text{CH}_3\text{O}$  is not known directly, it has to be determined indirectly.

Using the relation,

$$\text{IP}(\text{CH}_3\text{O}) = \Delta H_f^\circ(\text{CH}_3\text{O}^+) - \Delta H_f^\circ(\text{CH}_3\text{O}) \quad (14)$$

and taking from the literature<sup>36</sup> the values  $\Delta H_f^\circ(\text{CH}_3\text{O}^+) = 184$  kcalmol<sup>-1</sup> and  $\Delta H_f^\circ(\text{CH}_3\text{O}) = -0.5$  kcalmol<sup>-1</sup>, then,

$$\text{IP}(\text{CH}_3\text{O}) = 184.5 \text{ kcalmol}^{-1} \quad (8.00 \text{ eV})$$

Using this value and the value of  $\text{AP}(\text{CH}_3\text{O}^+)$  calculated in this work, then,

$$D(\text{CH}_3\text{O}-\text{H}) \leq 4.46 \text{ eV} \quad (102.85 \text{ kcalmol}^{-1})$$

The value of  $D(\text{CH}_3\text{O}-\text{H})$  can also be calculated by the cycle,

$$D(\text{CH}_3\text{O}-\text{H}) = \Delta H_f^\circ(\text{CH}_3\text{O}) + \Delta H_f^\circ(\text{H}) - \Delta H_f^\circ(\text{CH}_3\text{OH})$$

where the values of  $\Delta H_f^\circ(\text{H}) = 52.095$  kcalmol<sup>-1</sup> and  $\Delta H_f^\circ(\text{CH}_3\text{OH}) = -47.96$  kcalmol<sup>-1</sup> are taken from the literature. This yields

$D(\text{CH}_3\text{O} - \text{H}) = 99.56$  kcalmol<sup>-1</sup>, which is in good agreement with the value calculated using expression (13).

The bond dissociation energy  $D(\text{CH}_3\text{O} - \text{H}^+)$  can also be evaluated using the following expression:

$D(\text{CH}_3\text{O} - \text{H}^+) \leq \text{AP}(\text{CH}_3\text{O}^+) - \text{IP}(\text{CH}_3\text{OH})$  with the observed values of  $\text{AP}(\text{CH}_3\text{O}^+)$  and  $\text{IP}(\text{CH}_3\text{OH})$ . In this case,

$$D(\text{CH}_3\text{O} - \text{H}^+) \leq 1.45 \text{ eV (33.44 kcalmol}^{-1}\text{)}$$

The value of the bond dissociation energy for the ion is much lower than that of the corresponding molecule.

The bond dissociation energy  $D(\text{CH}_3 - \text{OH})$  may also be evaluated for comparison with  $D(\text{CH}_3\text{O} - \text{H})$ .

Using the expression

$$D(\text{CH}_3 - \text{OH}) \leq \text{AP}(\text{CH}_3^+)_{\text{CH}_3\text{OH}} - \text{IP}(\text{CH}_3)$$

where  $\text{AP}(\text{CH}_3^+) = 13.7 \text{ eV}$  and  $\text{IP}(\text{CH}_3) = 9.840 \text{ eV}$  from the literature<sup>36</sup>, then,

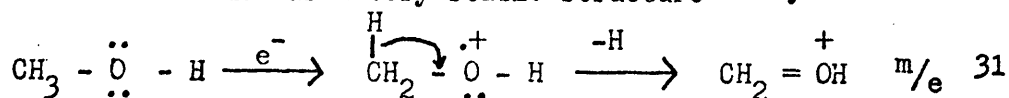
$$D(\text{CH}_3 - \text{OH}) \leq 3.86 \text{ eV (89.02 kcalmol}^{-1}\text{)}$$

Comparing this value with the value of  $D(\text{CH}_3\text{O} - \text{H})$ , it might be presumed that since the bond  $\text{CH}_3\text{O} - \text{H}$  is stronger than the bond  $\text{CH}_3 - \text{OH}$ , the abundance of  $\text{CH}_3^+$  ions would be greater than the abundance of  $\text{CH}_3\text{O}^+$  ions. This is not in fact the case, as is shown by the spectrum of methanol under standard conditions given in table 4.2.

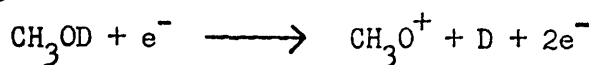
TABLE 4.2.Spectrum of Methanol.

m/e	relative abundance
12	0.33
13	0.72
14	2.4
15	13.0
16	0.21
17	1.0
28	6.3
29	64.0
30	3.8
31	<u>100.0</u>
32	66.0
33	0.93
34	0.14

The most abundant ion in the spectrum is  $\text{CH}_3\text{O}^+$  and  $\text{CH}_3^+$  is much less abundant. This is believed to arise from a rearrangement in which the oxonium ion is formed as a very stable structure<sup>62,63</sup>:



Using the observed value of  $\text{AP}(\text{CH}_3\text{O}^+)_{\text{CH}_3\text{OD}}$ , the bond dissociation energy  $\text{D}(\text{CH}_3\text{O} - \text{D})$  corresponding to the process:



can be evaluated.

$$\text{D}(\text{CH}_3\text{O} - \text{D}) \leq \text{AP}(\text{CH}_3\text{O}^+) - \text{IP}(\text{CH}_3\text{O})$$

$$\text{D}(\text{CH}_3\text{O} - \text{D}) \leq 4.71 \text{ eV} (108.62 \text{ kcalmol}^{-1}).$$

This value is larger than the value of  $\text{D}(\text{CH}_3\text{O} - \text{H})$  and this is assumed to be due to the difference in bond dissociation energy of the two bonds C-H and O-D, the latter being stronger. It would be expected that in the deuterated methanol the  $\text{CH}_3\text{O}^+$  would be less abundant than in the undeuterated case. This is confirmed by the relative abundances of the peaks  $m/e$  33,  $m/e$  32 and  $m/e$  31 in the spectrum of deuterated methanol, shown below:

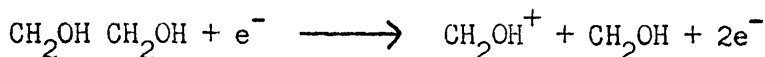
$m/e$	relative abundance
31	45.0
32	<u>100.0</u>
33	49.0

Thynne and Harland<sup>64</sup> have come to similar conclusions in the case of negative ions. In this case, it is suggested that  $\text{CH}_3\text{O}^-$  formed from  $\text{CH}_3\text{OD}$  has a smaller cross-section than in the case of the undeuterated methanol.

Using the value of the appearance potential of the ion  $\text{CH}_2\text{OH}^+$  in ethylene glycol, the bond dissociation energy  $\text{D}(\text{CH}_2\text{OH} - \text{CH}_2\text{OH})$



associated with the following process can be evaluated.



$$D(\text{CH}_2\text{OH}-\text{CH}_2\text{OH}) \leq \text{AP}(\text{CH}_2\text{OH}^+)(\text{CH}_2\text{OH})_2 - \text{IP}(\text{CH}_2\text{OH})$$

$$D(\text{CH}_2\text{OH}-\text{CH}_2\text{OH}) \leq 4.26 \text{ eV} (98.24 \text{ kcalmol}^{-1}).$$

This value is of the same order of the value  $D(\text{CH}_3\text{O}-\text{H})$  which supports the conclusion that the ion  $\text{CH}_3\text{O}^+$  really exists as the species  $\text{CH}_2\text{OH}^+$ .

Using this value, the heat of formation of the ethylene glycol was calculated by means of the following thermochemical cycle.

$$D(\text{CH}_2\text{OH}-\text{CH}_2\text{OH}) = 2 \Delta H_f^\circ(\text{CH}_2\text{OH}) - \Delta H_f^\circ(\text{CH}_2\text{OHCH}_2\text{OH}).$$

$$\Delta H_f^\circ(\text{CH}_2\text{OHCH}_2\text{OH}) \geq -99.24 \text{ kcalmol}^{-1}.$$

The difference between this value and the heat of formation of the ethylene glycol in the liquid phase<sup>65</sup>,

$$\Delta H_f^\circ(\text{CH}_2\text{OHCH}_2\text{OH})_{\text{liq}} = -108.58 \text{ kcalmol}^{-1},$$

may now be calculated.

$$\text{Difference} = |-108.58 + 99.24| = 9.34 \text{ kcalmol}^{-1}.$$

This difference, of the order of  $10 \text{ kcalmol}^{-1}$ , is the expected value for this type of compound.

Using the observed ionisation potential of the ethylene glycol and the appearance potential of  $\text{CH}_2\text{OH}^+$ , the indicated bond dissociation energy in the ion may be calculated.

$$D(\text{CH}_2\text{OH}-\text{CH}_2\text{OH}^+) \leq \text{AP}(\text{CH}_2\text{OH}^+) - \text{IP}(\text{CH}_2\text{OHCH}_2\text{OH}).$$

$$D(\text{CH}_2\text{OH}-\text{CH}_2\text{OH}^+) \leq 2.25 \text{ eV} (51.89 \text{ kcalmol}^{-1}).$$

This value is much lower than the bond dissociation energy in the neutral molecule, which means that the formation of the ion  $\text{CH}_2\text{OH}^+$  is achieved by initial ionisation of the glycol molecule and subsequent dissociation.

Bibliography (Chapter 4.)

1. P. Lenard, Wied. Ann., 1889, 37, 443.
2. J. Franck, Verh. d. Deutsche. Phys. Gesell., 1910, 12, 613.
3. G. Hertz, Wied. Ann., 1892, 55, 28.
4. P.T. Smith, Phys. Rev., 1930, 36, 1293.
5. J.T. Tate and P.T. Smith, Phys. Rev., 1934, 46, 773.
6. J.T. Tate, P.T. Smith and A.L. Vaughan, Phys. Rev., 1935, 48, 525.
7. D.P. Stevenson and J.A. Hipple, Phys. Rev., 1942, 62, 237.
8. D.P. Stevenson and J.A. Hipple, J. Amer. Chem. Soc., 1942, 64, 1588.
9. D.P. Stevenson and J.A. Hipple, J. Amer. Chem. Soc., 1942, 64, 2766.
10. J.H. Beynon, "Mass Spectrometry and its applications to organic Chemistry," Elsevier Publishing Co., Amsterdam, 1960, p.286.
11. P.F. Knewstubb, "Mass Spectrometry and Ion-Molecule Reactions," Cambridge University Press, Cambridge, 1969, p.22.
12. F.H. Field and J.L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, 1957, p.61.
13. J. Roboz, "Introduction to Mass Spectrometry," John Wiley and Sons, London, 1968, p.415.
14. C.A. McDowell in "Mass Spectrometry," Ed. C.A. McDowell, McGraw-Hill, New York, 1963, p.510.
15. R.E. Honig, J. Chem. Phys., 1948, 16, 105.
16. S. Geltman, Phys. Rev., 1956, 102, 171.
17. (a) G.H. Wannier, Phys. Rev., 1953, 90, 817.  
(b) G.H. Wannier, Phys. Rev., 1955, 100, 1180.
18. D.R. Bates, A. Fundaminsky, J.W. Leech and H.S.W. Massey, Phil. Trans. Roy. Soc. (London), 1950, A243, 93.
19. E.P. Wigner, Phys. Rev., 1948, 73, 1002.

20. (a) W.M. Hickam, R.E. Fox and T. Kjeldaas, Jr., Phys. Rev., 1954, 96, 63.  
(b) R.E. Fox in "Advances in Mass Spectrometry," Vol.I, Ed. J.D. Waldron, The Institute of Petroleum, New York, 1959, p.397.
21. W.B. Nottingham, Phys. Rev., 1939, 55, 203.
22. A.J.B. Robertson, "Mass Spectrometry," Methuen & Co., London, 1954, p.36.
23. J.D. Waldron and K. Wood in "Mass Spectrometry," The Institute of Petroleum, London, 1952, p.16.
24. P.T. Smith, Phys. Rev., 1930, 36, 1293.
25. H.D. Smyth, Proc. Roy. Soc. (London), 1923, A102, 283.
26. J.W. Warren, Nature, 1950, 165, 810.
27. F.P. Lossing, A.W. Tickner and W.A. Bryce, J. Chem. Phys., 1951, 19, 1254.
28. (a) J.D. Morrison, J. Chem. Phys., 1951, 21, 1767.  
(b) J.D. Morrison, J. Chem. Phys., 1954, 22, 1219.
29. (a) J.D. Morrison, J. Chem. Phys., 1963, 39, 200.  
(b) J.D. Morrison, Bull. Soc. Chim. Belges, 1964, 73, 399.
30. E.M. Clarke, Can. J. Phys., 1954, 32, 764.
31. P. Marmet and L. Kerwin, Can. J. Phys., 1960, 38, 787
32. (a) R.E. Fox, W.M. Hickam, T. Kjeldaas, Jr., and D.J. Groove, Phys. Rev., 1951, 84, 859.  
(b) R.E. Fox, W.M. Hickam, D.J. Groove and T. Kjeldaas, Rev. Sci. Instr. 1955, 26, 1101.
33. J.M. Williams and W.H. Hamill, J. Chem. Phys., 1968, 49, 4467.
34. R.W. Kiser, "Introduction to Mass Spectrometry and its applications," Prentice-Hall, Englewood Cliffs, N.J., 1965, pp.176-186.
35. M. Krauss and V.H. Dibeler in "Mass Spectrometry of Organic Ions," Ed. F.W. McLafferty, Academic Press, New York, 1963, p.145.

36. J.L. Franklin, J.G. Dillard, H.M. Rosenstock, J.T. Herron, K. Draxal and F.H. Field, "Ionisation Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, U.S. Government Printing Office, Washington, D.C., 1969, p.3.
37. J.L. Franklin, J. Chem. Phys., 1953, 21, 2029.
38. W.M. Scott, M.E. Wacks, J.D. Fitzpatrick and C. Steelink, 17th Ann. Conf. on Mass Spect., Dallas, May, 1969, p.442.
39. D.P. Stevenson, J. Chem. Phys., 1942, 10, 291.
40. G.C. Eltenton, J. Chem. Phys., 1942, 10, 403.
41. J.A. Hipple and D.P. Stevenson, Phys., Rev., 1943, 63, 121.
42. F.P. Lossing and A.W. Tickner, J. Chem. Phys., 1952, 20, 907.
43. H.D. Hagstrum, Rev. Mod. Phys., 1951, 23, 185.
44. (a) C.E. Berry, Phys. Rev., 1950, 78, 597.  
(b) H.I. Stanton, J. Chem. Phys., 1959, 30, 1116.
45. (a) C.R. Lagergren, Phys. Rev., 1954, 96, 823.  
(b) F.L. Mohler, V.H. Dibeler and R.M. Reese, J. Chem. Phys., 1954, 22, 394.
46. P.A. Finan, R.I. Reed and W. Snedden, Chem. and Ind., 1958, 1172.
47. F.P. Lossing, P. Kebarle and J.B. de Sousa, in Reference 20(b) p.431.
48. W.C. Price, Chem. Rev., 1947, 41, 257.
49. G.A. Junk and H.J. Svec in "Recent Topics in Mass Spectrometry," Ed. R.I. Reed, Gordon and Breach, London, 1951, p.85.
50. C.A. McDowell, Ind. Chim. Belge, 1954, 19, 713.
51. M.E. Wacks and V.H. Dibeler, J. Chem. Phys., 1959, 31, 1557.
52. G.G. Hall in "Advances in Mass Spectrometry," Vol.IV, Ed. E. Kendrick, The Institute of Petroleum, London, 1968, p.547.
53. M. Krauss in Reference 52, p.575.
54. F.P. Lossing, Can. J. Chem., 1972, 50, 3973.

55. (a) R.A.W. Johnstone and B.N. McMaster, J. Chem. Soc., Chem. Comm., 1973, 730.  
(b) R.A.W. Johnstone and F.A. Mellon, J. Chem. Soc., Faraday Trans. II, 1972, 68, 1209.
56. G.D. Flesch and H.J. Svec, J. Chem. Soc., Faraday Trans. II, 1973, 69, 1187.
57. C.D. Finney and A.G. Harrison, Int. J. Mass Spect. and Ion Phys., 1972, 9, 221.
58. (a) J. Jalonen, P. Pasanen and K. Pihlaja, Org. Mass. Spect., 1973, 7, 949.  
(b) P.C. Cardnell, A.G. Loudon, R. Mazengo, I. Russell and K.S. Webb in "Advances in Mass Spectrometry," Vol.VI, Ed. A.R. West, The Institute of Petroleum, London, 1974, p.41.
59. D.D. Perrin, W.L.F. Armarego and D.P. Perrin, "Purification of Laboratory Chemicals," Pergamon Press, Oxford, London, 1966.
60. E. Friedam, T.J. Gill and P. Doty, J. Amer. Chem. Soc., 1961, 83, 4050.
61. K. Watanabe, J. Chem. Phys., 1957, 26, 542.
62. L. Friedman, F.A. Long and M. Wolfsberg, J. Chem. Phys., 1957, 27, 613.
63. J.H. Beynon in Reference 10, p.347.
64. P.W. Harland and J.C.J. Thynne, Int. J. Mass Spect. and Ion Phys., 1972, 9, 253.
65. F.D. Rossini, D.D. Wagman, W.H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," NBS 500 - Part I, U.S. Government Printing Office, Washington, D.C., 1952.