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DIGITAL ANALYSIS OF MASS SPECTRA

ABSTRACT

The purpose of this thesis is twofold. A special type of signal is studied and methods for its reduction investigated. The results of this work are then applied to the automatic reduction of the trimethyllead mass spectrum with the aim of improving the information recovery from this signal, using modern data processing techniques.

The precision measurement of amplitudes must always provide some form of averaging or filtering. It is demonstrated that the results become increasingly sensitive to irregularities in the abscissa of the record, as the width of the averaging function increases. The continuity of the transition from a purely height sensitive calculation to an area sensitive calculation depends on the shape of the impulse response of the measuring arrangement. For all physical shapes, a least squares fit will lead to area sensitive amplitudes. These results have not been known in mass spectrometry or, to our knowledge, in other fields.

The mass spectrum is regarded as the convolution of an ideal line spectrum and a peak shape which is determined by the characteristics of the mass spectrometer and the associated electronics. The reduction presents essentially a problem in deconvolution. Although occasionally suggested in the literature, methods involving transformation to the frequency domain were not found to be useful. Thus it is necessary to carry out the analyses entirely in the time domain. Even then, methods requiring the use of derivatives of the spectrum, which have been successfully applied in special cases, usually suffer seriously from noise.

Correlation techniques are especially valuable for signals with a high noise content. Correlation is an integration in the time domain and corresponds to a general filtering process in the frequency domain. A close relationship between the correlation technique and a least squares method is emphasized.
The development of a practical procedure for this laboratory was part of the study. The trimethyllead group of the tetramethyllead spectrum is recorded in digital form on paper tape. At a constant sampling rate of two per second, about fifty readings per mass interval are recorded. The reduction of the paper tape record to relative isotopic abundances of lead has been automated, applying the experience gained from the general study. The saving in reduction time over former standard methods is substantial. There seems to be a real reduction in the standard deviations of individual peak measurements, but this does not exceed a factor of two.

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Field of Study: Mass Spectrometry

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J. S. Kirkaldy, D. H. Weichert and Z. Haq:


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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
in the Department
of
Geophysics

We accept this thesis as conforming to the
required standard

THE UNIVERSITY OF BRITISH COLUMBIA
September, 1965
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Date October 4, 1965
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CHAPTER I
INTRODUCTION

1.1 A Special Class of Signals

The general impact of the electronic digital computer on our society in the preceding one and one-half decades has been enormous and has had wide influence. Most branches of science and engineering have profited from the arrival of the stored-program computer which brought into the realm of practicality calculations formerly considered to be unmanagable. Some sciences have found more use for the computer than others.

In many of the geophysical disciplines a vast number of available data has long withstood a detailed analysis, but, with their large memory and great speed, modern computers are changing the picture drastically. This development is far from being complete, and the present study of digital processing of mass spectra is but one more example of the application of modern data processing procedures to a special class of signals encountered in geophysics and in other branches of science. The methods used have only become practical at this university during the past year.

Many different classes of signals are recorded in the natural sciences. The mathematical methods which are used to reduce and transform these recordings into a form which is more amenable to their physical interpretation are as
varied as their origins and appearances. In many cases Fourier series or integral analyses are used to extract the desired information from a set of data. If, for instance, the frequency content of a statistical sample from an infinite aperiodic signal is of interest, methods similar to the ones described by Blackman and Tukey (1958) are likely to be employed. If the record is thought to represent the effects of a superposition of several cyclic phenomena, the well-known methods of harmonic analysis comprehensively described by Bartels (1951) will prove useful.

A special class of signals often encountered in physics and geophysics has its origin in a discrete set of events, each giving rise to a signal which can be represented mathematically by a delta function suitably broadened according to the physical phenomenon. When measured and recorded, more or less overlapping peaks of finite width and amplitude will be obtained, and the shape of each peak will include the effects of the measuring device and method. Often it is possible to advance sound arguments and evidence that this shape remains essentially unchanged over the range of observation. The record can then be thought of as the convolution in the observational variable of the series of delta functions and the peak shape. Accordingly, the output is given by three sets of parameters which are the positions of the input spikes, their magnitudes, and the parameters determining the peak shape. In addition, a certain amount
of noise will always be mixed with the recorded signal, and signal-to-noise ratios may vary from very small to very large values. The problem on hand may not require the explicit determination of all three sets of parameters; the requirement on precision may also differ from case to case. The methods employed will vary with the objective and with the noise content of the signal.

Mathematically, the process of inverting the convolution, or removing the overlapping of adjacent peaks, is very simple if the peak shape is known. It could be achieved for example, by a point-by-point division of the Fourier transform of the record by the transform of the peak shape. Because of the ever-present noise our knowledge, both of the true convolution and of the peak shape, is only approximate, and small errors in the representation of the record may lead to gross deviations in the results.

In the simple case, in which the noise level is negligible and the peak positions are well known, a system of equations would be set up and solved, using the dominant features of the record. If the noise level is not quite so low or the peak locations not known, a greater number of data may be combined by the application of the principle of least squares or of another criterion to obtain the best fitting parameters. Correlation techniques have been widely used for similar purposes, particularly when the signal-to-noise ratio is very low. There is no clear-cut separation between these methods; for
instance, a least squares fit could be interpreted as a correlation method as we shall see later. Neither is there a clear distinction between methods used for the determination of one or the other set of parameters. In many practical applications the best technique to be used for the particular objective will be found by a cut-and-try procedure.

The automatic extraction of information from a special signal of the class described above forms the objective of this thesis. Before considering mass spectra, however, it is useful to give a few examples of other signals belonging to the same category.

1.2 Examples of Related Signals

In spectroscopy a finite number of possible atomic or molecular transitions lead to a line spectrum which is usually recorded photographically. The positions of the lines give information about the energy differences of the initial and final atomic or molecular states, while the relative intensities of the lines reveal the probabilities of the transition causing that line. The lines will always have a finite width. This is partly due to such things as the grain size of the film or the exposure times, but also reflects phenomena not related to the measuring equipment. To the extent that the line shapes are the same, this is the class of signal referred to above. The estimate of the line position will be somewhat arbitrary if the reduction of the data is done manually, and objective methods of finding the
most consistent peak locations are described in the literature (eg. Wilson, 1965).

A similar line spectrum is obtained in X-ray crystallography, where both, photographic and counting techniques are used for the recording of the intensity of the diffracted beam. Here again the relative position of the various peaks are the parameters which are to be determined with a high precision. The estimates of the line locations on a photographic plate by a human observer are highly subjective (Pike, 1958). On the other hand, if more objective methods are used for spectra with slightly asymmetric line profiles, different techniques will also lead to inconsistent estimates and uncertainties (Wilson, 1965).

The yields of nuclear reactions are studied with the aid of some kind of pulse analyser. There is reason to assume that the output of the measuring device due to a monoenergetic beam of particles has the form of a Gaussian, possibly with some non-Gaussian tailing (McWilliams et al., 1962; Heiberg, private communication). The multichannel analyser spectrum will therefore be a superposition of a series of such Gaussian lines whose positions and heights are determined by the energy and yield of product particles, and thus is a further example of the type of signal with which we will be concerned.

An example with a low signal-to-noise ratio is found in seismology. Here, underground structures and layers of different elastic constants are inferred from records of
reflected seismic waves. If it can be assumed that the profile of the wave reflected from a single interface is (at least approximately) independent of the media on either side, and independent of depth then the seismogram could be considered to be made up of an unknown number of strongly overlapping reflections from unknown positions, while their amplitudes would be determined by the relative properties of the reflecting layers. The comparison of artificial seismograms with true records has, for instance, been considered by Delaplanch (1963) and a review of correlation techniques which are well suited for such cases was given by Anstey (1964).

1.3 A Particular Example: The Tetramethyllead Mass Spectrum

While in other fields of research the questions arising from the problem of inverse convolution have been discussed in more or less detail, the problem has found little attention in the field of mass spectrometry. Two different objectives usually guide the design of mass spectrometers. The precise measurement of mass differences requires a spectrum with well defined peak positions which are sometimes achieved instrumentally with a sacrifice of the stability of the peak heights. A precise measurement of isotopic abundances on the other hand, calls for a high degree of reproducability of the peak heights, while the mass differences may either be known or of lesser interest. The mass spectrometry group in the Geophysics laboratory of The University of British Columbia has for the past seven years been concerned with the
precise measurement of the relative abundances of the lead isotopes of masses 204, and 206 to 208.

The isotopic composition of lead has long been used to estimate the age of minerals containing lead, using a knowledge of the decay schemes of uranium-235 and -238, and of thorium, whose endproducts are the lead isotopes 207, 206 and 208, respectively. On the basis of several hundred isotopic compositions, such as those collected by Russell and Farquhar (1960), different geochemical models have been suggested. Since the precision of the then-available analyses was insufficient to evaluate the models, R.D. Russell and a group of his graduate students set up the present research program.

As early as 1960, Kollar reported isotopic analyses of lead obtained from a new gas-source mass spectrometer built in this laboratory, which were relatively more precise than any other analyses of the kind. Kollar achieved this precision by the careful attention given to details in the design and construction of the electronic circuits and measuring system of the new machine, and to the introduction of an intercomparison and looping technique (Kollar, 1960). Three years later, Ostic (1963) further reduced the relative error in intercomparisons of the lead isotope ratios of different samples to about 0.05 percent using Kollar's spectrometer with improved sample handling procedures and data reduction. Both workers obtained their raw data partly by visually reading a rotating dial and recording the readings by hand,
and partly by measuring values from a continuous chart record of the spectrometer output. The dial was mounted on the shaft of a ten-turn potentiometer whose setting is proportional to the ion current being measured. Kollar first pointed out that this shaft would be very suitable for recording the whole spectrum in a digital form. Thus one of the objectives of this thesis is the description of a system of obtaining and handling such digital spectra and their completely automatic reduction to isotopic abundance ratios. The development of the necessary computer programs for the reduction and the investigation of related problems has occupied not only a considerable part of the writer's efforts but also in the neighbourhood of 200 hours of computer time (120 hours of IBM-1620 time; 50 hours of IBM-7040 time).

The advantages of automation are threefold: to eliminate the strain imposed on the operator, to eliminate operator bias and possible errors in reading the dial, and to increase and improve the information retrieved from the record by the use of high speed data processing equipment. The first point is unquestionably desirable. The possibility of operator errors can also readily be accepted. The dial is subdivided into 2-degree intervals, and while observing the dial and attempting to make a good estimate of the average reading on top of a peak in terms of fifths or tenths of one division, the operator may easily misread or misrecord one of the more
significant digits. Operator bias may be small but is hard to dispute. While even on a stationary scale an estimate to the nearest tenth of a division of approximately one millimeter will lead to disagreement between different persons, the additional uncertainty of a moving scale and the necessity of choosing the proper time for the reading increases differences in judgement of different operators. On the high sensitivity ranges on which the noise on the dial is of the order of one or two dial divisions, operator bias may easily be one half of a division. If the operator tends to read negative peaks (valleys between the peaks) in a similar way, the bias introduced may be still greater.

Despite the high resolution obtained with the spectrometer in this laboratory earlier authors directed their attention towards an evaluation of, and correction for, the contribution of the ion beam from one mass to the signal recorded at neighbouring mass positions. It was shown that this tailing was pressure dependent, and an empirical correction was applied to the measured peak heights. If all samples could be analysed at exactly identical pressures, the errors introduced in the intercomparison by incorrect peak tailing correction might be quite small; however, differences in composition and purity of the sample often prevent the use of identical operating pressures.

It now becomes clearer how the third objective of digitizing and automating the reduction of the mass spectrometer
output is to be achieved. Using high speed electronic data handling systems which are becoming more generally available, the data can be manipulated in a way which was not practical until a short time ago. In this way and with more sophisticated methods improved recovery of information can be obtained from the output.

The three distinct sets of parameters of this class of signals were stated to be the peak shape, the peak positions and the peak heights. Although the latter are of predominant importance in our work, the others are of general interest and in any case are needed for the reduction of the spectrum. They will be discussed in order in the subsequent chapters. Although the general approach will always be remembered, the guiding thought will be the application of interest in this laboratory, namely, the reduction of the lead trimethyl portion of the tetramethyllead spectrum.

1.4 Previous Computer Applications to Mass Spectra and Similar Records

1.4.1 Matrix Inversion. The usefulness of digital electronic computers for the reduction of mass spectrometric data has been pointed out as early as 1951, for instance, by King et al. (1951) or by Young (1952). However, these authors restrict the use of the computer to the inversion of the matrix obtained from spectra composed of several complex ion groups. The input data for the calculation were manually read and recorded, and later transferred to punched cards.
About the same time Collins (1952) reported from Toronto a similar reduction of the trimethyllead spectrum which has served as the basis for our present procedures. The Pb(CH\(_3\))\(_3\)\(^+\) spectrum is complicated by the related ion groups Pb(CH\(_3\))\(_2\)CH\(_2\))\(^+\), Pb(CH\(_3\))\(_2\)(C\(^{13}\)H\(_3\))\(^+\), and Pb(CH\(_3\))(C\(^{13}\)H\(_3\))\(_2\)\(^+\). Thus measurable ion currents are found for each of the masses 248 to 255. It has been found convenient to find approximate values for the carbon-13 contribution and hydrogen-loss probability and then to proceed with the inversion by iteration. A computer program which performs this calculation and related statistical analyses, has been developed over the past 11 years. It was first written in 1955 by R.D. Russell for a Ferranti electronic computer at the University of Toronto. Around 1960 it was translated and extended by J.L. Allard for use on an Alwac IIIE at this university. After two further adaptions it is now in use with an IBM 7040, and it is estimated that about 1500 isotopic compositions have been calculated with its aid.

A step towards automation was made by Fritts and Peattie (1956), who manually set a wire on the chart record at the top of each peak, and then operated a switch to print the digitized peak heights on prepared calculation sheets. A very similar method in which the data are directly punched onto cards has recently been introduced in the laboratory of J.C. Reynolds at the University of California.

Three years later Dudenbostel and Klaas (1959) described three automated data collection systems in which again only
selected points of the spectrum are recorded digitally. This is done by programming the accelerating voltage in one case and by recording all maxima above a certain level in another system. The concern of these authors always appears to be a saving in operator time for commercial routine analyses. The same is true for a solid state digitizing system for mass spectrometers described by Thomason (1963) which uses sophisticated computer logic-circuitry. The output of the spectrometer is sampled at high frequency and interpreted automatically. When a peak has been indicated by a reading less than or equal to the previous one, the circuitry will expect another 5 readings to be less than the previous ones before the value is recorded as a true peak. This is similar to the removal of high frequency noise by a numerical filter, as used by this writer (Chapter 3).

1.4.2 Fully Digitized Records. The first attempts to extract additional information by not only recording selected values of the spectrum, but recording and using the whole record, were made in X-ray analysis work and nuclear reaction analysis. Keller and Segmüller (1963) measured complete X-ray line profiles by means of a pre-programmed step scan. The intensity data were taken by the fixed count method and punched onto paper tape, together with such pertinent information as counting time and reflection angle. To estimate the background these authors plot their data on-line on the output typewriter of an IBM 1620 computer, using an enlarged scale for the tails. The
computer operator then decides from these plots the background level and feeds this information back into the computer. Bases are interpolated linearly, and tails are extrapolated by the formula \( y = \frac{a}{x} + \frac{b}{x^2} \) in some special cases. This procedure has features in common with the methods used by the present writer: however, the above authors then proceed to Fourier-analyse their data.

McWilliams, Hall and Wegener (1962) have applied the principle of least squares to the data obtained from charged particle energy analysers for a "consistent treatment of partially resolved peaks". They have the advantage of a theoretical basis for the use of a Gaussian peak cross section, and thus are able to fit a sum of Gaussians to the spectrum, leaving the amplitudes of the peaks, their positions and halfwidths unspecified. Because the unknowns do not appear linearly in the observation equations, a Taylor expansion up to the first derivatives is used, often leading to very unstable normal equations. This instability has forced the authors to make additional assumptions, such as adding conditional equations on peak positions, assuming simple relations between the halfwidths, or limiting the fit to only part of the spectrum at one time.

The present writer's approach has been similar to the methods of these writers, but differs substantially in its objective and in the assumptions that can be reasonably made. McWilliams, Hall and Wegener compare, for instance, the effect
of substituting a Lorentzian peak shape and obtain a difference of 3 percent for the value of a critical parameter. Lead isotope studies cannot afford a discrepancy of this magnitude in the peak amplitudes.

1.5 Conclusions

It appears then, that a completely automatic reduction can be achieved by two distinctly different methods. The main disadvantage of the systems of Thomason and of Dudenbostel and Klaas is the complex logic circuitry required for the detection of relevant peak and base values. Also, there is no way of reevaluating the whole spectrum at a later time, since only the values reported by the system are preserved. The system must be able to decide quite accurately where a peak has occurred and what its value was. It cannot do so without waiting some preset time interval during which it must constantly sample and test the output; therefore the system also needs an appreciable memory.

The second approach by Keller and Segmueller, involves electronics consisting essentially of a counter which advances the detecting unit by one increment when a preset number has been reached. Since very little logic is required and the memory for only one complete reading is needed, the recording system should be considerably simpler. Once all the information contained in the spectrum is recorded digitally any chosen technique of recovery can be applied with the aid of the sophisticated and fast logic system in the form of a
computer, now accessible to most modern research laboratories. After reviewing this material, one cannot help but conclude that there is ample room for extension of these ideas in the field of mass spectrometry.
2.1 The Existing Measuring System

2.1.1 Output. The major lead trimethyl ion currents of masses 249, 251, 252 and 253 atomic units, which must be measured with a relative precision of a few hundreds of one percent, are of the order of $10^{-10}$ to $10^{-12}$ amperes; the minor peaks, 250 and 254, range from $10^{-12}$ to $10^{-14}$ amperes. This current escapes through a $10^{11}$ ohm resistor and the voltage developed across it drives a servo amplifier. The system is essentially a null device and the feedback voltage is proportional to the collected ion current. Five different sensitivity ranges are available, which are selected by operating a push button switch. On the range of lowest sensitivity (designated as number five) the full voltage of a reference battery is applied to the end taps of a motor-driven potentiometer. This voltage is attenuated by approximately a factor of three for each lower range (higher sensitivity). The reciprocal of these attenuation factors are in proportion to the scaling factors for the readings on the various ranges.

The output from the system consists of a shaft rotation of the ten-turn high-precision potentiometer. A permanent continuous record of an analysis is written by a conventional Honeywell-Brown chart recorder which is driven by a secondary, mechanically coupled potentiometer. When recording manually
as in the past, the most significant digit is read from the chart while the fractions of one turn would be read from a 3-inch dial mounted on the common shaft of the two potentiometers.

2.1.2 Precision. The precision of the final measurements is determined by several factors all of which have been studied in the past. The stability of the supplies was discussed by Kollar (1960) and by Kollar and Russell (1960), while the voltage coefficient of the Victoreen Hi-Meg resistor was investigated by Whittles (1960a and b). The linearity of this type of precision potentiometer (Helipot 7600 series) is given by the manufacturer as 0.025 percent of full scale, and the ones used have not been worse than 0.017 percent. The response of servo systems, with particular reference to the one used in the measuring system of the mass spectrometer of this laboratory, has been described in detail by Whittles (1960a), by Stacey (1962) and by Stacey and Russell (1965).

If the system is well designed, the precision of the reading must not be the limiting factor of the attainable overall precision. When the dial readout is used the scale is estimated to one tenth of a 2-degree division. Its precision however, would not be expected to be better than about one fifth of a 1.3 mm division. When measuring a typical peak of one half full-scale height this amounts to about 0.02 percent.

2.3.3 Bandwidth. In the above-cited reference Stacey gives the results of the measurements of the response of the
separate parts of the servo system and of the closed-loop stabilized amplifier. According to his estimates, the overall bandwidth of the measuring system is from zero to about three cycles per second, which seems to be sufficient for a reasonable scan speed of approximately 2.5 mass units per minute. It is often preferable to express the frequency response characteristics of a measuring system in terms of an equivalent averaging time. The inverse Fourier transform of the characteristic function can then be considered as a weighting or averaging function which is applied to the input signal. If one approximates the system response by \( \exp(-f^2/\omega^2) \), which has a half width of three cycles per second, the averaging function is proportional to \( \exp(-18\pi^2\omega^2t^2) \), for which the width is about one hundred milliseconds. This is a reasonable estimate of the intrinsic averaging time of the measuring system.

2.2 The Digitizing System

2.2.1 The Encoder. In the measuring systems presently used in this laboratory the potentiometer shaft position is directly proportional to the feedback voltage which is proportional to the ion current. Both the mechanical and electrical outputs are suitable for digital conversion; either choice has points in its favour. The mechanical link was chosen because of price considerations and, more important, because it permits simple servo-division techniques useful in ratio recording of mass spectra. This application of electro-mechanical systems has been of interest to our
laboratory for some time (cf. Stacey, Russell and Kollar, 1965). Because a suitable 10-turn, 1000 count/turn encoder was commercially available (Perkin Elmer Model 10/1000), this proved to be a convenient choice. This choice of encoder also satisfies the mechanical restrictions. The automated output system should not adversely affect the operation of the existing measuring system. The requirements are a relatively low moment of inertia and small friction. Although the friction requirement does not appear to present a problem, some manufacturers specify that the shaft must be clamped during readout, which may take as long as 75 msec; others increase the load torque by a factor of 50 or 100 when the encoder is engaged. Either specification is completely unacceptable for our system. The requirement of low moment of inertia appears to be harder to obtain. The aluminium dials previously used on the mass spectrometer had about 7.6 cm diameter, and were 1.6 mm thick, with a moment of inertia about 150 gm-cm$^2$. Digitizers with rotating-disc commutators would have an inertia of about this magnitude, but mechanical coupling of several discs in a multi-digit readout will lead to substantially higher values.

The encoder offered by the Perkin-Elmer Corporation seemed to satisfy all our demands and was therefore purchased. The instrument is advertised as a one-brush, absolute (against incremental) encoder. The patented use of only one brush is made possible by additional electronic circuitry in the readout
system. Readings are taken without clamping the shaft. The moment of inertia is given by the manufacturer for the Model 10/1000 as 0.5 oz-in.$^2$ (90 gm-cm$^2$). The maximum starting torque is given to be 0.35 oz-in. (25 gmf-cm), but this writer found it to be only 11.5 gmf-cm. Compared to the measured starting torque of 112 gmf-cm of the potentiometer this is negligible. The quoted moment of inertia of the encoder is about one half of that of the dial arrangement.

The digitizer was at first connected to the shaft of the potentiometer by a tight fitting steel sleeve, which was held in place by a set screw. This was found to be unsatisfactory as it soon became evident that a small amount of slippage could not be avoided. It was suspected, in this connection, that the small residuals obtained by Ostic (1963) after removing the downward trend of the peaks by fitting a third or fifth order polynomial may have been caused by very small amounts of slippage between dial and shaft. The minimum requirement for the shaft connections is the provision of a flat for the set screw; drilling and tapping of the shaft or the use of a tapered pin are still preferable.

2.2.2 Electronics. The complete system, from encoder to paper tape punch, was supplied by the Vernistat Division of the Perkin-Elmer Corporation. A block diagram is shown in Figure 2.1. Table 2.1 gives part numbers and prices of the separate units. The encoder provides input to the readout. This unit contains register, buffer storage and BDC outputs.
Table 2-1 Components of Perkin-Elmer Digital recording system.

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Model number</th>
<th>Description</th>
<th>Price (US$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perkin-Elmer</td>
<td>10/1000</td>
<td>Ten-turn, 1000 counts per turn encoder</td>
<td>560.-</td>
</tr>
<tr>
<td>Perkin-Elmer</td>
<td>4 R S</td>
<td>4-digit readout, without display, input capacity 24 bits</td>
<td>1275.-</td>
</tr>
<tr>
<td>Perkin-Elmer</td>
<td>T/Pl</td>
<td>Punched tape programmer, Output: 8 codes/word, 8 characters/word maximum</td>
<td>2120.-</td>
</tr>
<tr>
<td>Teletype Corporation</td>
<td>BRPE 11</td>
<td>Paper tape punch, 110 operations/sec. maximum</td>
<td>900.-</td>
</tr>
</tbody>
</table>
Figure 2.1 Block diagram of Perkin-Elmer digital recording system.
The punched-tape programmer contains the sequencing and control circuits, the parity driver and the punch gates and drivers. The unit is capable of handling a maximum word length of eight characters; each character can contain up to eight bits of information. The power supply of the programmer is also used to generate auxiliary data by a contact closure of the shunt and scan drive switches of the mass spectrometer.

The original record-command arrangement was slightly modified. Readout is now initiated by a 4 volt, 1 msec pulse obtained from a unijunction relaxation oscillator, whose frequency is adjustable from approximately 0.2 cycles/sec to 5 cycles/sec. To establish the linearity of the time base for the digitized spectrum, the stability of the readout command was tested at the desired frequency of 2 cycles/sec. Table 3.2 gives a typical series of intervals between consecutive readings; there was no significant drift over a period of one hour. The bias resistors were chosen to obtain temperature compensation of the device (G.E. Transistor Manual, 1964 edition, page 313). A hot solder iron held a few millimeters away from the unijunction transistor would raise the period typically from 0.495 to 0.498 seconds. Warming with the fingertips had no noticeable effect. Supply voltage stability is obtained by placing a Zener diode across the clock.

2.2.3 The Paper Tape Record. For the recording of the collected data three alternatives were considered. Recording
Table 2-2 Stability of period of readout command. The series of intervals in columns (a) and (b) were recorded an hour apart. Intervals were spaced about two seconds.

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th></th>
<th>b</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>.5010 seconds</td>
<td>.5006 seconds</td>
<td></td>
</tr>
<tr>
<td></td>
<td>.5007</td>
<td>.5007</td>
<td></td>
</tr>
<tr>
<td></td>
<td>.5010</td>
<td>.5012</td>
<td></td>
</tr>
<tr>
<td></td>
<td>.5007</td>
<td>.5010</td>
<td></td>
</tr>
<tr>
<td></td>
<td>.5009</td>
<td>.5008</td>
<td></td>
</tr>
<tr>
<td></td>
<td>.5008</td>
<td>.5008</td>
<td></td>
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<tr>
<td></td>
<td>.5010</td>
<td>.5006</td>
<td></td>
</tr>
<tr>
<td></td>
<td>.5010</td>
<td>.5012</td>
<td></td>
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<tr>
<td></td>
<td>.5010</td>
<td>.5012</td>
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<td></td>
<td>.5008</td>
<td>.5010</td>
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<td></td>
<td>.5008</td>
<td>.5012</td>
<td></td>
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<td></td>
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<td>.5009</td>
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<td>.5012</td>
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<td>.5008</td>
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<td></td>
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<tr>
<td></td>
<td>.5008</td>
<td>.5008</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>.5092</td>
<td>Average</td>
<td>.50082</td>
</tr>
</tbody>
</table>

Table 2-3 Comparison between average and least-squares-adjusted bases. Only four significant digits are recorded by the system.

<table>
<thead>
<tr>
<th>Average Bases</th>
<th>Adjusted Bases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shunt</td>
<td>2</td>
</tr>
<tr>
<td>60553</td>
<td>48331</td>
</tr>
<tr>
<td>60826</td>
<td>48361</td>
</tr>
<tr>
<td>60438</td>
<td>48317</td>
</tr>
<tr>
<td>59847</td>
<td>48260</td>
</tr>
<tr>
<td>60020</td>
<td>48287</td>
</tr>
<tr>
<td>59587</td>
<td>48237</td>
</tr>
</tbody>
</table>
on magnetic tape was rejected for the present because of high
cost, but should be considered for the future. The data
could be punched onto IBM cards, in which form they are
ready for the present input facilities to the electronic
computer at this university. However, the card punches
available have punch speeds of only about 20 codes per second,
which was considered marginal for the proposed data sampling
rate of 1 to 3 per second. Furthermore, the dead time of 250
milliseconds, while one card is ejected from the punch station
and the next one fed into it, would also necessitate a more
elaborate electronic system for buffer storage. The third
alternative of using a punched-paper tape output combines
both the advantages of relatively low cost and high enough
punching speed for any sampling rate that might be desired
for our purpose.

The format of the eight level tape which is now used
is kept as simple as possible. Of the maximum eight
characters per word only six are wired and used at present.
The first four digits contain the setting of the potentiometer in standard IBM BCD paper tape code. The sensitivity
range on which a measurement has been made is punched into
levels 1-2-4 of column five. The direction of scan is superimposed onto the same column, a hole in the 0- and X-levels
denoting downmass and up-mass scan respectively. All tape
codes generated in this way are standard or special characters
of the IBM code. For instance, the letters J to N represent
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upmass scan on ranges 1 to 5; a slash, and the letters S to V are used for downmass scan on the five ranges. Thus level 8 is not used at all in column 5 of each word, and therefore various combinations are available to allow the operator to feed in additional information, should this become desirable. The end of each word of information is indicated by a punch in level EOL, the standard IBM code for "end-of-line", which is generated by the programming unit. The punched-tape programming unit also generates odd parity which uses up one level of the available eight.

At first frequent parity errors in the tape caused inconvenience, but were traced to slight mechanical misadjustment of the Teletype high-speed punch. The rare occurrence of tape errors is now mostly confined to the last column of auxiliary data and appear to be caused by switching transients.

2.3 The Computer

Although the mass spectrometer output is not directly linked to the Computing Center, the computer is a vital part of the data reduction system. The core of the present facilities available to the user is an IBM 7040, with an IBM 1402 card input and a 1403 printer, both "on-line" at the present time. Several magnetic tape units are available for input of data from the users' own tape. Serial disc storage has just become accessible to the user at the time of writing. Although MAP, COBOL and Fortran IV compilers are presently available, this writer has written all his programs in Fortran.
The capacity of the memory of the central processing unit is \(8^5\) words of 36 bits fixed length. Somewhat less than 20,000 words of this is presently used for the reduction programs and the system nucleus, leaving about 12,000 words for data storage. A typical mass spectrometer run has about eight downmass and upmass scans, but more should be allowed for. Since it is inconvenient and time-consuming when programming in Fortran to handle one spectrometer reading as a single word, one data word is stored in two locations; the first is used for the shaft position and the second for both the shunt number and scan direction. At a sampling rate of two readings per second the storage requirement for six pairs is about 12,000 locations. Although this would just be available, it was decided not to reduce a whole run simultaneously but to read and calculate each pair separately. Another important reason was the frequent occurrence of parity errors in the first punched-paper tapes. To deal with these in a convenient way an extra location serving as additional checkbit and as a marker for switching transients was set aside for each word of data. This made the available storage inadequate

* Computer efficiency was not a main objective of this study. Obviously packing techniques, probably using the MAP language, could remove this restriction.
for handling a whole run.*

2.4 Preprocessing and Filtering of Data

2.4.1 Sampling Rate and Quantization. Digitization of a continuous function involves both a quantization in time and in signal amplitude. Although the best representation of the signal will be achieved by the closest spacing of data points, economical considerations impose a constraint on both the sampling rate and the number of significant figures recorded.

In our system, all decisions necessary for the reduction of the record are to be left for the main computer. Therefore it is necessary to preserve all information contained in the output signal. From a purely intuitive approach one could estimate a sampling rate such that the fastest occurring changes of the output are reasonably well represented by the recorded points. For instance, one could attempt to determine

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* Machine time may be another consideration. The basic machine cycles of the 7040 are of the order of a few microseconds. However, for many data processing applications the lower limit of the handling time is determined by the input and output. The reduction programs were designed with due attention to as much overlap of input and calculation time as possible. About seven seconds are required to read from cards the data for one pair, and the reduction time is somewhat less than twenty-four seconds, but could be reduced. The output speed is of no practical concern, since the amount of output data is relatively negligible. Magnetic tape is used for intermediate data storage; the extra writing and reading time is small. When off-line input becomes available overall computing time will be cut appreciably. At present, the total computer time required for the reduction of one pair is about 34 sec.
the interval between samples so that a linear, or a parabolic interpolation between neighbouring points does not depart significantly from the continuous chart record. A much better foundation for the selection of a sampling rate is found in sampling theory (Suesskind, 1957; Blackman and Tukey, 1958). In effect, the results of the theory show that, in order to completely recover the original signal, the highest occurring frequency must at least be sampled twice in one period. Physical signals, however, do not have a finite frequency content. The part of the signal spectrum lying above that frequency corresponding to twice the sampling period will be reflected and superimposed onto lower frequencies, and the original signal can only be recovered approximately. The best one can do is to choose the folding frequency (and therefore the sampling rate) high enough to include all frequencies lying in the pass band of the system. As stated previously, the bandwidth of our measuring system reaches to about three cycles per second. However, a power spectrum analysis was made on a typical record, and it was found that frequencies above one cycle per second do not contribute significantly to our records (see Figure 2-2). (This is of course not true for switching transients, most of which were eliminated from the record before analysis.) The sampling rate was therefore chosen as two per second. This gives about ten to twelve readings across the top of a peak, and, of course, also satisfies the intuitive requirement of adequate representation in regions of rapidly changing signal (cf. Figure 2-4).

The number of the recorded significant figures will affect the precision of the measurement. Again, as in the
Baselines have been subtracted before the Fourier analysis, so that the record goes smoothly to zero at both ends of the scan. Switching transients were interpolated linearly between adjacent parts of the record. For integration purposes the record was represented by a parabolic segment between three consecutive points. Rapid changes in the spectrum are not shown. The importance of the spectrum lies in the fact that its salient features disappear beyond about 0.6 sec\(^{-1}\).
preceding section, an obvious intuitive argument leads to a satisfactory estimate of the introduced error, but a more secure estimate is obtained from quantizing theory. The modern approach (Linvill, 1951) makes use of the distribution function of the signal and its Fourier transform. The theory shows that the errors have a zero average and a mean square of $q^2/12$, where $q$ is the quantization step, and are the same for all frequencies. This is equivalent to the well-known Sheppard's correction in statistics for grouping of data. It could be obtained in a very elementary manner by considering the second moment about the center of a quantization interval, of a data distribution, which is constant over the range of that interval. For the chosen 4-digit readout the rms error is therefore about .006 percent.

Irregularities in the exact placement of the recorded points will introduce additional errors in the representation of the signal. However, variations of the period of the readout command of our system were shown to be small; it may therefore suffice here to say that timing inaccuracies can be treated as additional quantization errors (Suesskind, 1957).

2.4.2 Data Continuation. The ten-turn digitizer in our system is not provided with stops at the ends of its range. While the potentiometer does have stops, these are not set at the end taps, and overshoot can and does occur frequently. The collected raw data will therefore often contain discontinuities which are corrected while the data are read into the
computer. At the same time this procedure permits clamping of the digitizer and potentiometer shafts in any position. This is very desirable because an exact alignment of the zeros is difficult and time consuming. The procedure is essentially based on the sampling rate used in recording. With two readings per second, the observed maximum separation of two consecutive readings was one third full-scale. According to the combination of a number of symbolic switch positions inside the computer, which are set automatically at the beginning of each new set of data, the machine will add or subtract a full scale reading from the data or leave them unchanged. A block diagram of the switching system is shown in Appendix II.

2.4.3 Elimination of Transients. Switching from one sensitivity range to another introduces transients into the records which bear little relationship to the signal. Many subsequent calculations however, depend on an uninterrupted record, and a simple procedure was therefore developed which eliminates these transients while the data are read into the computer. The method is necessarily empirical and is based on the observation of a number of such transients recorded at different sensitivities. It is found that the transient time does not appreciably depend on the height of the step, e.g. a transient on shunt-2 dies out within 3 sec, regardless

---

* Although the range changing circuitry does not strictly use electrical shunts, the terms "shunt-selector" and "shunts" are used regularly in the laboratory to denote the range-switch and its setting.
whether the operator switched down from shunt-5 or from shunt-3. The observed times are found to be so closely linear to the shunt numbers, that it was found convenient to define and eliminate from the data a transient time of 4 seconds after each shift to shunt-2, and 0.5 sec less for each higher shunt. This contains a safety margin of 1 sec over the observed 3 sec on shunt-2.

After the baseline values have been subtracted from the data and the result has been multiplied by the corresponding shunt factors, the data for the transient times are interpolated linearly between the adjoining values, in order to obtain an uninterrupted record; a note is made so that interpolated values can be recognized later. This is necessary, for instance, in a least squares fit, in which the transient data are assigned zero weights. Higher order interpolations were tested but showed no advantages.

2.4.4 Baselines. In the past, when reducing a chart record by hand, baselines were established at each end of a single scan, without checking the relative position of the bases on the different shunts. However, a simple relation exists between the bases. When reducing automatically the additional labour of checking and adjusting the bases is negligible, but will eliminate errors of the order of the quantization step and lessen the effects of friction which is doubtlessly small but nevertheless present. The following will illuminate the procedure.
A transistor preamplifier of gain 0.7 is employed as impedance matching device between the 10^{11} ohm ion-current leakage-resistor and the measuring system (Russell, Otic and Stacey, 1964). The preamplifier is operated with a small but finite feedback voltage in the absence of any signal. On different sensitivity ranges this voltage will be obtained by different potentiometer settings which are recorded as baselines. If the potentiometer can be assumed to be linear near its zero setting (without significant error due to finite wire spacing), the feedback voltage for a fixed bias is proportional to the product of potentiometer setting times the shunt factor, for all ranges. Therefore, a plot of shaft position against the reciprocal of the shunt factor should be a straight line. In practice the fit is usually so good, that a graph of the size of this page does not show the deviations. In fact, the deviations that are observed are generally smaller than the quantization step of the digitizer and could be wholly due to quantization errors. Table 2-3 gives a comparison between a series of average base values and the corresponding values after adjusting them in the least squares sense.

2.4.5 Filtering. When inspecting a record, high frequency noise of small amplitude is always noticed, but the eye automatically averages over this noise and the relevant features of the spectrum are found with ease. For the electronic computer this is more difficult. If, for
instance, it is looking for peaks it will note all maxima regardless of significance. A simple means of reducing high frequency variations is the methods of curve smoothing or numerical filtering. Filter theory has been discussed thoroughly in the literature (e.g. by Blackman and Tukey, 1958). Special attention to the filtering of geophysical data was given by Holloway (1958). The equivalent of filtering in the frequency domain is achieved by constructing a new time function from the original by forming an autoregressive series or a linear moving combination.

In the case of the autoregressive series the weighted average of a number of points of the data is substituted for the central point. The calculation is repeated with the center of the weight function moved to the next data point, thus using some of the previously smoothed points. The operation can be expressed as a convolution of the original function and the weight function. The transfer function of such a filtering process will always be complex i.e. a phase shift will be present which introduces asymmetries into the original record.

In a linear moving combination only values of the original data series are used to calculate the filtered data. The phase shift is strictly proportional to frequency for symmetric weight functions, and therefore gives a single time delay, which can be made zero. For an averaging function of \(2p + 1\) points with weights \(a_p\), the filtered data will be
\[ z_n = \sum_{m=-p}^{p} a_m y_{n+m} \]  \hspace{1cm} (2.1)

which is recognized as a convolution. Therefore the response of the filter is

\[ \frac{Z(f)}{Y(f)} = \sum_{m=-p}^{p} a_m e^{-i\omega m \Delta t} \]

\[ = 1 + 2 \sum_{m=-p}^{p} a_m \cos(\omega m \Delta t) \]  \hspace{1cm} (2.2)

where \( \Delta t \) is the spacing of the data.

A very good approximation to the shape of the transfer function can be obtained by calculating the response of the continuous envelope of the weighting function. For equal weighting over an averaging interval of length \( 2T \) the frequency characteristic is then approximately the familiar diffraction pattern, \( \sin(\omega T)/\omega T \), except for a constant. Some authors, for instance Holloway (1958), dislike an equal weighting because of the negative sidelobes of the diffraction pattern and prefer to use, for instance, binomial weighting whose transfer function approaches a Gaussian curve.

The need for a high frequency filter for our data becomes clear from Figure 2-3 which shows the vicinity of the peaks of mass 248 to 250. Note that the peak tops of mass 249 and 250 have been moved down to include them in the graph. Various filters were investigated in the course of this work. A three-point or five-point averaging function alone proved not to be enough to eliminate noise problems encountered in later reductions, and a consecutive application of a three-point
Figure 2-3 Vicinity of 249-peak of trimethyllead spectrum, unfiltered
Figure 2-4 Vicinity of 249-peak of trimethyllead spectrum, filtered.
and five-point average was adopted. This corresponds to a single weighted function with weights 1,2,3,3,3,2,1. Its frequency response is shown in Figure 2-5. The repeated square filter eliminates the multiplication by the weights and is therefore preferable from a computational point of view over a simple filter. The region of the record of Figure 2-3 is again shown in Figure 2-4 after application of the above filter. Note that the peak shape is extremely well preserved.

When selecting a filter for our type of data it is important that the width of the total averaging function is less than the width of the peaks, because this width varies slightly throughout the spectrum. Too wide a window will result in relative height loss of the narrower peaks. This effect is considered in more detail in Chapter 5.

It is sometimes stated that after the application of a smoothing function to the original data, only the midpoints of non-overlapping averaging ranges need be retained. In some cases this procedure may be justified. However, it involves an irreversible loss of information, since for a complete algebraic inversion of the filtering process one needs all points of the filtered series.
Figure 2-5 Frequency response of numerical filter used for smoothing.
CHAPTER 3
THE PEAK SHAPE

3.1 Introduction

The general approach to the extraction of optimum information from a signal consisting of overlapping responses to a discrete input must provide for a determination of the shape of the noise-free response to an impulse. For the more specialized objectives of mass spectrometry, i.e. mass or abundance measurements, the peak shape plays only a secondary role, but an approximate knowledge of this shape will be required for the precise determination of the other sets of parameters.

For the purposes of isotope ratio measurements a knowledge of the peak heights at a few integral mass units on either side of its center will usually be needed, even for instruments of high resolving power. This is of course the most pressing reason for our interest in the peak shapes. In this laboratory it was soon recognized that empirical curves could be drawn showing the relationship between the height of the peak tails and pressure. Occasionally peak heights for nonintegral mass distances were desired, but interpolations used were dictated by convenience rather than a precise knowledge of the peak shape.

Other reasons for the interest in the peak shape exist. For example, previous studies in this laboratory were
concerned with an analysis of the performance and errors of
the closed loop feedback system of the ion-current measuring
arrangement, using Laplace transform methods (Whittle, 1960a).
These studies gave rise to the search for a mathematical
description of the peak, and several such representations
leading to simple transforms were employed. A crude repre­
sentation satisfies this requirement. In other spectra of
physical interest which show a much lower resolution the
position of the peaks are not so easily determined as in our
records. Several methods exist to reduce the effects of
overlap and define the separate peaks more sharply. All of
these methods utilize some a priori knowledge about the
peak shape.

This writer has used least-squares analyses to improve
the knowledge of the pressure dependent tailing correction.
For this purpose a continuous expression is needed at least
for some parts of the peak. In a later chapter the possibility
of applying a least squares fit to the complete spectrum is
discussed. Although this is not practical with our present
experimental arrangement the appropriate modifications in
instrumentation should probably be undertaken in the future.
A complete mathematical description in terms of a few
parameters, preferably continuous in all the parameters,
would be very desirable.

3.2 The Origin of the Peak Shape and its Variation over
the Spectrum

Morrison (1963) has compared a mass spectrometer with a
communication channel: the input for this channel corresponds to a series of infinitely sharp lines, one for each mass present in the ion beam. During its passage through the channel, the input signal will be convolved consecutively with the impulse response functions of the separate parts of the mass spectrometer. In the source, the small but finite spread in energy of the ionizing electrons results in a corresponding spread of the emerging ion beam. Passage through the accelerating field and exit slit will give the cross section of the beam its dominant features. The current which is finally collected is the integral over that part of the beam which is seen through the collector slit. Further broadening and distortion may be caused by the response characteristics of the electronic measuring system. For our system however, this is negligible. Stacey and Russell (1965) have shown that the bandwidth is sufficient to transmit without distortion signal frequencies up to about three per second while this writer has shown in Chapter 2 that signal frequencies above one per second are negligible. Apart from noise originating in the electronic system, the recorded signal should therefore represent faithfully the collected ion current.

Several small effects may contribute noticeably to the final peakshape: reflection from the edges of the exit slit may scatter a small proportion of the emerging ions away from the beam axis, while another small fraction may
suffer collisions within the analyser tube with residual gas molecules. The common result of these and other mechanisms is a spreading of a small fraction of the beam.

The position of a beam relative to the collector slit is a simple function of the magnetic field strength. However, when the spectrum is scanned the field is not simply related to the magnetizing current, nor is the current simple proportional to time. The first relationship is governed by the inductance of the magnetizing coils and by the hysteresis of the magnet, while the second is a consequence of the usual nonlinear scan current drive. The peaks become visibly narrower during one scan, corresponding to an increase in the rate of change of flux in the magnet gap, along the steeper part of the hysteresis curve. The effect is considered when the peak shape and from it the pressure corrections are calculated. The simplest way to account for this nonlinearity is a polynomial expansion of the peak positions and a subsequent one-to-one mapping of the time axis onto a flux (actually $B^2$) axis. The computer program doing this mapping is referred to in Appendix II.

The usefulness of knowing the overall impulse response of the instrument depends to a large extent on the assumption that this peak shape (apart from noise) does not change over the range of the lead trimethyl spectrum. The most obvious possible cause for a change of cross section of the ion beam is, of course, space charge. Its effects are usually
assumed to be negligible and a simple calculation can demonstrate this*. There are other effects which probably do produce slight changes in peak shape. The ions of different masses follow slightly different trajectories, and the fringe effects of the magnetic field should also show some dependence on the field strength since we operate near saturation. However, the differences between trajectories are of the order of millimeters, passing through a field whose dimensions are several hundred times larger, and the proportional change of the magnetic induction is only one-half of the corresponding relative change in mass. It therefore seems to be quite legitimate to ignore the possibility of a significant variation of the beam shape and with it the peak shape over the range of the spectrum, provided that the square of the magnetic induction is considered to be the independent variable.

3.3 Mathematical Representation of the Peak Centre

3.3.1 The Trapezoidal Peak. As pointed out above, the dominant shaping process of the ion beam emerging from the

* Around mass 250, the 5000 accelerating volts impart to the ions a velocity of 65,000 meters per second, equivalent to a flight time of 15 microseconds. At a maximum ion current of about 10^-10 amperes, the ion-density in the beam is 10^4 per meter along its length. Assuming a uniform beam cross section of .1 by 10 mm, the average volume density is around 10 ions per cubic millimeter, or the average separation one half millimeter. The spreading by electrostatic repulsion at a distance of this order is about 0.1 micron during the transit time, insignificant compared to the original average separation of about 500 micron.
source takes place during its passage through the exit slit (Figure 3-1). The assumption that this slit is uniformly "illuminated" with ions leads to a trapezoidal peak when observed through a wider collector slit.

Its appearance will vary greatly, depending on the ratio of the widths of the collector and exit slit. If they were identical, the peak would be triangular, having its vertex at the point of exact coincidence of the beam and collector slit. For an exact measurement of abundances this arrangement would not be very satisfactory, but for a precise measurement of peak position it would be more useful, and this writer has used a closely analogous numerical method for the precise definition of the peak locations (cf. Chapter 4). If the ratio of the slit widths is different from one a trapezoidal peak will result. In our instrument the collector slit is 0.5 mm and the exit slit 0.1 mm. Some broadening due to the $R\alpha^2$ term was estimated by Kollar (1960) as 0.5 mm, so that the ratio $w_c/w_1$ would be somewhere between five and three. One half of a typical peak, without its long tail is shown on the right of the center line in Figure 3-3. Remembering, that the measuring system should be capable of following much sharper corners at peak tops and bases than

* The linear, second order aberration is equal to the radius of curvature of the ion path, $R$, times the square of the half-angle of divergence, $\alpha$, of the beam at the exit slit.
Figure 3-1 First Order Focusing Mass Analyzer

Figure 3-2 Mass Spectrogram Representing Peaks for Masses $M$ and $M + \Delta M$.
(After Kollar, 1960)
Figure 3-3 Comparison of experimental peak and error function

ERROR FUNCTION
(cf. Equation 3-2)

EXPERIMENTAL
253-PEAK,
FILTERED

MASS SEPARATIONS

.5 .4 .3 .2 .1 .1 .2 .3 .4 .5
are observed, it is quite evident that the beam cross section is not uniform, not even to a first approximation which ignores any tailing effects. Nevertheless, this form of peak representation has served to study the output position error of different types of servosystems.

3.3.2 The Trigonometric Peak. Because of the poor agreement of the trapezoidal peak and the actually observed spectrum and because the discontinuities at the corners introduced oscillatory responses in the analysis, both Whittles (loc. cit.) and later Stacey (1962), following a suggestion of R.D. Russell, considered another discontinuous definition of the peak, being unity along the top and having sides of the form $y = \frac{1}{2} - \frac{1}{2} \cos(\pi(x-x_0)/(x_1-x_0))$.

Compared with a typical peak, the corners of this trigonometric form are not sharp enough, and it soon goes to zero, which the real peaks do not. However, the choice of the trigonometric representation was mainly dictated by the simplicity of its Laplace transformation which the above authors used for the system analysis, and for this purpose was quite adequate.

3.3.3 The Gaussian Beam Shape. Consideration of the rectangular slit, and the assumption of a rather slowly varying distribution of the beam before reaching the slit led to a clearly incorrect trapezoidal peak. The only other acceptable assumption which one can make without getting involved with scattering mechanisms is a Gaussian beam shape. Let the beam shape be $g = I_0 \exp(-\frac{(x-x_0)^2}{2s^2})$, with the
origin at some arbitrary point, and with effective half-width $s$. For a collector slit width $w_c = 2s/r$, the recorded ion current will be

$$i(x) = \int_{x-s/r}^{x+s/r} I_o \exp\left(-\frac{(z-x_0)^2}{2s^2}\right) dz \quad (3.1)$$

where $x$ is the point of the spectrum which is centered on the collector slit. The integral (3.1) is easily expressed in terms of the error function or its complement, for instance,

$$I(X) = I_o \left[ \text{erfc}\left(\frac{(x-x_0)r-s}{\sqrt{2}sr}\right) - \text{erfc}\left(\frac{(x-x_0)r+s}{\sqrt{2}sr}\right) \right] \quad (3.2)$$

In Figure 3-3 the left half of a peak of the form (3.2), with $r$ approximately one fifth, is shown in juxtaposition to a peak obtained from an actual spectrum. The similarity is surprisingly good, but the difference still discernable. A closer fit could be obtained with a more careful selection of the error function parameters. However, the experimental peak shape varies so strongly with operating conditions that different parameters would have to be used for each run.

One serious objection to the representation of equation (3.2) is the often observed asymmetry of the top edges and slopes. If a refinement of the mathematical representation were desired, this asymmetry could be obtained by the substitution of a few Hermitian polynomials for the coefficient $I_o$ in
equation (3.1); however, for the present this is unnecessary since only the representation of the peak tails will be required.

The other objection to the use of error functions for the description of the peak is the behaviour of the observed tail shape. Although Figure (3-3) does not show it, the tailing is clearly recognizable in the original record up to distances of one mass separation (cf. Figure 3-6); in the downmass direction it still amounts to a few hundreds of one percent at distances of two mass units. Whether the long tail is caused by that small fraction of the beam which is scattered by collisions in the analyzer tube or by other causes is immaterial, it cannot be included in a simple way in the description of the major part of the peak. Because of the importance of the tailing correction in the high precision intercomparison of lead isotope abundances the peak tail deserves special attention.

3.4 The Peak Tail

3.4.1 Review of Previous Work. Kollar (1960) calculated pressure correction factors at one and two mass distances from the baseline rises under the small peaks. He assumed the scattering to be the same in the upmass and downmass directions, and reports a linear relation between these corrections and the background pressure. Ostic (1963) recognized that the calculated factors in the upmass and downmass directions are consistently different, but for
correction purposes he nevertheless averaged both values. He confirmed Kollar's pressure relation and found the one and two mass factors to be approximately given by

\[
x = 9 \cdot 10^{-4} p
\]
\[
y = 2.5 \cdot 10^{-4} p
\] (3.2)

\(p\) is the indicated pressure in microtorr (1 microtorr = 10^{-6} mm Hg). Particularly the two-mass factors show a considerable scatter. Whittles (1964), who analysed microgram quantities of lead at comparatively high pressures and who was therefore particularly interested in pressure scattering corrections, first showed that the differences in upmass and downmass corrections may lead to more consistent results for samples analysed at different pressure. For lower pressures his relationships corresponding to those in equation (3.2) are about

\[
x_d = 12 \cdot 10^{-4} p
\]
\[
x_u = 6 \cdot 10^{-4} p
\]
\[
y_d = 5 \cdot 10^{-4} p
\]
\[
y_u = 1 \cdot 10^{-4} p
\]

The \(x\) and \(y\) designate tail heights at one and two mass units; the indices \(u\) and \(d\) differentiate between the up and downmass corrections.
3.4.2 New Data on Pressure Dependence. With the use of automatic reduction of the data, the pressure factors, as defined and used in previous work, can now be calculated on a routine basis for every scan. Although the assumptions made in their calculation are not entirely free from the criticism of inconsistency, this writer wishes to present some new results as evidence in support of later work. For reference purposes, the equations used by Ostic (1963) for the calculation of the pressure factors are given here:

\[
\begin{align*}
    b_9 &= w a_9 + y d a_1 \\
    b_0 &= x u a_9 + x d a_1 + y d a_2 \\
    b_4 &= x u a_3 + y u a_2 \\
    b_5 &= x u a_4 + y u a_3
\end{align*}
\]

(3.3)

where the \( b_i \) are the heights of the tailing measured under the respective peaks, between a curve, interpolated between the minima adjacent to the peak, and the baseline, and the \( a_i \) are the peak heights of masses 249 to 253. The \( w \) accounts for the contribution to the baseline rise under the 249 peak due to this peak itself. Numerically, \( w \) has been assumed to be about twice the average one mass factor. The last two equations can be directly solved for \( x_u \) and \( y_u \). From about 150 scan pairs calculated by this writer, the average, \( y_u \), is only insignificantly different from zero, as can be seen from Table 3-1. Each value in this table is an average over all pairs of a run. The value of \( x_u \) is then very closely equal
Table 3-1 Tail heights from standard pressure calculation. The heights at one and two integer mass distances in the upmass and downmass directions are given. (in units of $10^{-4} \times$ (height at peak center)).

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<th>1-up</th>
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to $b_4/a_3$. When calculating manually, the baseline under mass 254 is drawn with a French curve, while in machine reduction the harmonic mean of the minima adjacent to mass 254, weighted according to the distance from the peak center, is employed*. This corresponds to a hyperbolic interpolation between the minima. Clearly, the choice of the French curve and of the operator will bias the value of $x_u$ as does the particular choice of interpolation in the machine calculation. The interpolation under the 254 peak is no problem. The difference between a straight line and a hyperbola is small. However, any error in $x_u$ will affect $y_u$ slightly. Providing $y_u$ is considerably smaller than $x_u$, equation (3.3) shows their relationship to be approximately

$$\frac{dy_u}{dx_u} = \frac{-a_4}{a_2 d_x} \frac{dx_u}{dx_u} = \frac{dx_u}{30}$$

Figure 3-4 shows the $x_u$ values obtained by this writer. A comparison is only possible with Whittles' (1964) curves since previous work does not differentiate between upmass and downmass factors. For one microtorr we obtain a tail height of $2 \times 10^{-4}$, which is about one third of Whittles' values. The writer believes that this difference is caused by opposite bias in the two interpolation techniques.

Values for the downmass tailing are obtained from the

$$y_0 = \frac{y_1 y_2 (d_1 + d_2)}{(y_1 d_1 + y_2 d_2)}$$

where the $d_i$ are the distances of the minima from the peak center.

* $y_0 = y_1 y_2 (d_1 + d_2)/(y_1 d_1 + y_2 d_2)$, where the $d_i$ are the distances of the minima from the peak center.
Figure 3-4 Tail heights from standard calculation.
Figure 3-5 Tail heights from a least-squares fit.
first two equations of the set (3.3). Because of the relative magnitude of the major peaks, with $a_9:a_1:a_2:a_3$ about 1:16:16:36, the assumption made for the value of $w$ and the substitution of $x_d$ for $x_u$ are of little consequence. However, the use of the downmass base as reference and the assumption of only two significant downmass tail values is more serious and may tend to hide the true shape of the downmass tailing. It has been realized for some time that the base values at the downmass end of the trimethyllead range are often higher than at the upmass end. Whittles believed that the downmass tail might extend to about eight mass units. The downmass tailing corrections obtained using Ostic's equations (3.3) are presented in Figure 3-4 and included in Table 3-1. The present writer obtained lower values than Whittles for both $x_d$ and $y_d$. Whittles drew his line for $y_u$ with an initial slope of about $1 \times 10^{-4}$ per microtorr, whereas we have already concluded that it does not differ significantly from zero.

3.4.3. The Mathematical Representation of the Tail. In some of the following sections it will be necessary to have a suitable mathematical expression for the peak tailing in our records as a function of distance from the peak center. Unless a detailed study of the varied causes of the tailing effect is made it is not possible to give a functional form which has a theoretical basis. It is then best to take the usual recourse to empirical expressions, and a selection of
a particular form will be based not only on an acceptable fit to the available data, but also on convenience. The properties which are required of the peak representation are few: it should go to zero or take negligible values at a finite distance from the peak center, its general shape must fit the tail directly adjacent to the strong 251 and 253 peaks and, finally, its values must be consistent with the tail heights. The most obvious form is a series in inverse powers of the distance from the peak center, or some other point closer to the steep sides of the peak. To avoid the pole of this series, a rather broad Lorentzian* of very small amplitude could be superimposed on the central peak. This seems to be the best choice, if the transition to the steep slopes are obtained by the error function. For the purposes of the following sections however, we do not intend to use a functional representation of the central peak and the sharp transition should therefore be achieved in a continuous fashion by the expression for the peaktails. After some experimentation we suggest the use of a simple hyperbolic formula,

\[ y = \frac{F(x-Z)}{(x-P)}, \quad Z_{\text{down}} < x < Z_{\text{up}} \quad (3.5) \]

with different constants, \( F, P, \) and \( Z \), for the upmass and the downmass tails. The parameter \( Z \) forces the tail to zero.

* \[ y = \frac{1}{1+x^2/w^2} \]
values at a finite distance from the center, beyond which it is assumed to remain zero*. Since the physical meaning of $P$ and $P'$ is not easily visualized, the equivalent values for the scattering coefficients at one mass and two mass units will normally be reported.

In this thesis we shall have no occasion to require a parametric form for the central portion of the peak. For use in the tail fitting programs a complete peak shape is obtained by copying the highest peak of the spectrum down to a level between about 5 to 2 percent, where it is still quite steep, and then extrapolating, using equation (3.5) for the upmass and downmass tail separately. The hyperbolic form is particularly well suited because it gives a good transition between the steep slopes of the sides of the peak to the gently sloping tails.

As an example of the fit of the function (3.5) to shapes of the peak tail obtained from the record, Figure 3-6 shows the upmass portion of the tail of mass 253, interpolated graphically under the peak of mass 254. The heights of the crossed points were calculated from equation (3.5), with the parameters adjusted to fit the curve at one half mass and at one mass unit, and reaching the zero level at two and one half mass units.

* This definition precludes the possibility of negative peak values, which could be caused by secondary electron emission. If this does occur its distribution should be independent of the tail shape, and additional parameters would be needed to describe the effect.
Figure 3-6 Fit of a hyperbolic tail to experimental data.
While in Figure 3-6 the choice of points for the determination of the parameters was dictated for ease of illustration, calculations have shown that the shape of the tail becomes less sensitive to small details at the base of the 253 peak, and the transition becomes more continuous, if a point between 2 and 5 percent of the peak height is chosen as the starting point for the extrapolation instead of the one half mass point, as shown. This is illustrated by Table 3-2. It lists the peak heights at two and three mass units from the peak as functions of the height and position of the copied point from which the tail is extrapolated. It can be seen that the shape varies only little with this point if it is about 5 percent.

3.4.4 The General Approach to the Least Squares Fitting of the Tails. For reasons which will be explained in more detail in a later chapter (cf. Chapter 5) a least squares fit to the complete spectrum, treating peak heights, positions and tail parameters as independent variables is not useful for our purposes. However, in our efforts to obtain more information on the pressure tailing, a least squares fit which is confined to a selected number of points of the lowest few percent of the spectrum appears to be a valuable tool. Several methods have been tried experimentally by the writer all of which give the same general result. In the following we will only describe a rather unusual and general approach and some of its results, and a simpler and less time consuming procedure which could be incorporated in the standard reduction program.
Table 3-2: Variation of tailshape with the extrapolation parameters. Note the insensitivity to R and d.

- $Z_{\text{down}} = -4$ mass units,
- $d$ = distance from peak center of beginning point of extrapolation, in fractions of mass separations,
- $R$ = ratio of beginning point to height at one mass distance,
- $D_{2,3} = \text{fractional peak height at 2 and 3 mass units (x 10^6)}$,

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<th>$D_3$</th>
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In section 2.4.4 a relation between the baselines for different sensitivity ranges was shown to exist. In section 3.4.2 it was implied that the distance to which the tailing was measureable is not well known and that the so-called base values, especially at the low-mass end of the spectrum, probably still represent small ion currents. It is therefore suggested that the location of the true baseline should initially be included as a set of unknown parameters into the least squares analysis. Three parameters have to be allotted for the determination of the baselines. According to section 2.4.4, the base line position on the \( i^{th} \) shunt will be given by

\[ B_i = b_0 + b_1 / R_i \]  

(3.6)

where \( b_0 \) and \( b_1 \) are constants. Because of the slow decay of the bias voltage term \( b_1 \), another parameter has to be included, leading to equation

\[ B_{i,n} = b_0 + b_{10}/R_n + nb_{11}/R_n \]  

(3.7)

where \( B_{i,n} \) is the base value for the \( n^{th} \) point of the spectrum, and \( R_n \) is the shunt factor for that point.

In terms of the ion beam intensities represented by a vector \( \mathbf{a} \) and a peak shape represented by a vector \( \mathbf{p} \), the spectrum will be the convolution \( \mathbf{p} \star \mathbf{a} \) (analogous to the continuous case). Then each point in the observed spectrum should fit the equation

\[ y_n = (\mathbf{p} \star \mathbf{a})_n / R_n + b_0 + b_{10}/R_n + b_{11}n/R_n \]  

(3.8)
The vector $\mathbf{p}$ includes a description of the peak and its tails. Here we are interested in base lines and tails which influence most the readings between the major peaks. Therefore it is sufficient to fit equation (3.8) to the data only in the portion of the spectrum for which the ion currents do not exceed about one per cent of the highest peak. This excludes most of the three major peaks, which would otherwise dominate the sum of deviations in any least squares procedure. The shape of the mass 253 peak is used together with tails of the form given in equation (3.5) to specify $\mathbf{p}$.

Since the parameters determining $\mathbf{p}$ appear non-linearly and discontinuously, the only unknowns for which (3.8) can be solved directly are the three b's. For $N$ data points, these are the $N$ equations

$$b_0 + (1/R_n)b_{10} + (n/R_n)b_{11} = y_n - (\mathbf{p} \mathbf{a})_n / R_n, \quad n = 1, N \quad (3.9)$$

which are reduced to three equations by multiplying from the left by the transpose of the matrix of coefficients of the left hand side (Jordan, 1961, vol. I, p. 668; also cf. Section 6.5). The resulting equations in matrix form are

$$
\begin{bmatrix}
N, \sum 1/R_n, \sum n/R_n \\
\sum 1/R_n, \sum 1/R_n^2, \sum n^2/R_n \\
\sum n/R_n, \sum n^2/R_n, \sum n^2/R_n^2
\end{bmatrix} \begin{bmatrix}
b_0 \\
b_{10} \\
b_{11}
\end{bmatrix} = \begin{bmatrix}
\sum \hat{y}_n \\
\sum \hat{y}_n / R_n \\
\sum \hat{y}_n n / R_n \\
\end{bmatrix} \quad (3.10)
$$

where $\hat{y}_n$ has been used for the residual $y_n - (\mathbf{p} \mathbf{a})_n / R_n$. 
While the upmass and downmass zeros of the tails are held fixed, estimates for the pressure corrections are now obtained by minimizing the sum of the squares of the residuals, using a procedure similar to the one described by Ostic, Russell and Reynolds (1963). To minimize the squared-error sum with respect to both, upmass and downmass parameters simultaneously, this sum would have to be calculated and equations (3.10) solved for nine points in each iteration. Then the minimum of the three-dimensional paraboloid interpolated between the nine points must be found, leading to non-linear equations for the corrections of the parameters. This is avoided by varying only one parameter at a time.

Least squares calculations for different assumed combinations of upmass and downmass zeros show a preference for short tails in both directions, but no sharp minimum with respect to the zeros has been found. However, the tail heights at one mass unit do not vary significantly with reasonable changes in peak length, and the upmass values are always smaller than the downmass ones. Depending on the initial estimates of the tail heights and the trial point separation the procedure sometimes converges to physically unacceptable values, or an excessive number of iterations may be required for satisfactory convergence. The technique is therefore not thought to be suitable for routine methods.

3.4.5 A Simplified Least Squares Fitting of the Tails.
The best fitting bases produced by the program described above
are consistently close to the base values as calculated and used in the present reduction program (cf. section 2.4.4). An increase in the stability of the solutions could therefore be achieved by using the partially reduced data for a least squares fit. In addition, the time requirement could be cut to more acceptable values by including fewer points. For instance, only all halfmass points of the smoothed record could be included in the fit. The baseline will now only be a small correction reflecting the uncertainty of the tail length. It can be represented by

\[ B_n = b_0 + nb_{11} \] (3.11)

If it is correct that the upmass tail attains zero values within 1.5 to 2.5 mass units, the upmass end of the spectrum should be essentially zero, and \( b_{11} = -b_0/N \). There is now only one of the normal equation left, namely

\[ (1 - n/N)b_0 = \sum Q_n \] (3.12)

which has to be solved for each trial point.*

* An estimate of the standard deviation of the fitted parameters can be obtained from the curvature of the curve of the sum of the squared errors plotted against one parameter, while the other is held constant, by the expression

\[ \text{St.Dev.}_{n+1} = (2Q_0/d_2 + (d_1/d_2)^2)^{1/2}d_1/d_2 h/(N-r)^{1/2} \] (3.13)

\( N \) is again the number of data points and \( r \) the number of fitted parameters. \( Q_0 \) is the sum of the squared errors for the middle estimate in any iteration; \( h \) is the spacing of the trial points, and \( d_1 \) and \( d_2 \) the first and second differences of the \( Q \)'s. Equation (3.13) is derived on the assumption that the sum of the squared errors reaches double its minimum value at points which are one standard deviation away from its minimum,
The results of this simplified least squares analysis are very similar to the results of the more rigorous treatment, thus justifying the simplifications. The stability is increased, but the number of iterations for convergence is still large if the initial estimates are not close to the optima. Convergence is assumed and the calculation stopped when the one mass factors change by less than three percent, or if the sum of the squared errors changes by less than one tenth of a percent. Again, short tails in both directions are preferred by this least squares analysis, but a distinct minimum is now found for an upmass zero of about 2.2 mass units. In the downmass direction a minimum was only found in one particular case for a tail length of about 3.5 mass units. Considerable changes in the assumption of the downmass zero change the magnitude of the one-mass pressure correction by less than twenty percent, a negligible amount. Figure 3-5 gives the pressure factors obtained by this method. A comparison with Figure 3-4 shows that both one-mass factors are higher than their counterparts calculated by the standard method. Far more important, as we shall see in Chapter 5, is the fact, that the tail heights at two downmass are given by both calculations as close to 0.02 percent per microtorr. The cause of the difference in the one-mass factors is believed to be the bias and that the sum can be approximated by a parabola up to these distances. (cf. Ostic, Russell, Reynolds, 1963) Stirlings central difference formula to second order terms is then used. (cf., eg. Willers, 1948, p.106).
for small values of the hyperbola used for the interpolation of base lines. The least squares results are therefore favoured by the writer.

3.5 Conclusions

At least a limited knowledge of the peak shape occurring in signals of the type considered is needed for their reduction. Sometimes it will be possible to express this shape in mathematical form on theoretical grounds. Alternatively, an isolated peak must be obtained and its shape described by empirical functions.

Consideration was given in this chapter to a mathematical description of the complete peak shape obtained from the mass spectrometer in this laboratory. Because of the various factors contributing to the final peak shape more than one term will have to be used for a complete representation. Error functions appear to describe the central peak portions well, while a Lorentzian or another form of hyperbolic tailing must be superimposed to describe the contributions to the shape of that small fraction of the ion beam which is spread over a wide range.

The peak tails are distinctly asymmetric. In the upmass direction a simple calculation and the method of least squares, using a hyperbolic tail shape, agree well and indicate that the tailing effect becomes negligible at about two mass distances from the center. Although in the downmass direction direct evidence is less conclusive, it seems established, that the
tail is not shorter than three mass-units and not longer than five.

The magnitude of the tailing effect varies approximately linearly with pressure over the range of interest. The values for the tail heights suggested by the writer are

\[ D_3 = 0.7 \times 10^{-4} \]  
\[ y_d = 2 \times 10^{-4} \]  
\[ x_d = 8 \times 10^{-4} \]  
\[ x_u = 4 \times 10^{-4} \]  
\[ y_u = 0 \times 10^{-4} \]
CHAPTER 4

PEAK POSITIONS

4.1 Introduction

The locations of the peaks form another set of unknowns in the type of signal considered in this thesis. Theoretical considerations may or may not predict the number of peaks and give some idea of their spacing. In general, several possibilities are recognized. The noise level may be relatively low and the peaks well resolved and sharp, striking the observer's eye and presenting little difficulty for their recognition by the dataprocessing system. If the peak tops are broad and possibly asymmetric, the precise location will be judged differently by different observers and the electronic computer needs a more elaborate routine for judging the placement of the peaks. If the resolution is lower, smaller peaks will begin to disappear into the shoulders of higher neighbours, and the computer as well as the human analyst will be increasingly less able to identify the peak position. As the noise level increases peak recognition will become more difficult in all above cases, until the peaks are submerged in the noise, becoming invisible.

Recorded signals may range anywhere between the described possibilities, and the chosen methods for exact peak locating will be as varied as the appearance of the signals. For high noise levels some filtering process will be the initial
suggestion, and the optimum will often be found to be a matched filter, corresponding to a cross-correlation with the peak shape which must then be known a priori. The record which is of special interest in this thesis, has relatively low noise levels, the resolution is good, but exact peak positioning is difficult for the electronic computer because of rather broad peak tops with an ill defined center.

This chapter will call attention to other techniques which have been used or suggested in mass spectrometry and similar fields and relate them to this particular application. After considering a purely empirical definition of peak position we shall discuss various procedures connected with the idea of deconvolution in the time domain*. A correlation technique which has been adopted for our purposes will then be presented, and finally a combination of this technique with the deconvolution methods will be suggested.

4.2 Least Squares Interpolation

In many practical cases, amongst them our own, the approximate peak positions are relatively easy to recognize or are known. The simplest and most obvious method of a consistent definition of the peak location is the least squares fitting of some continuous curve to the data points, and letting the peak positions be given by the maximum of this curve.

* It is still understood that strictly speaking the independent variable is the square of the magnetic induction rather than time.
Without any additional information or theoretical justification for the adoption of a particular analytic form, the parabola would be chosen as the simplest function. It is symmetric and one would therefore suspect an inherent bias in the locations of asymmetric peaks thus determined. This is indeed so, and Wilson (1965) shows that the bias in the location is proportional to the square of the range of observations used in the least squares fit, and to the ratio of third over second derivatives. The method could obviously be expanded to higher order fits which would eliminate the bias, although some assumptions about the peak shapes may have to be made. In the case of our spectra the peak tops are not suitable for a valid expansion in only a few terms of a power series. However, the simplest variant of this method, a parabolic interpolation between three points, will be usefully employed in section 4.6 in dealing with a cross-correlation of the spectrum.

4.3 Multiple Differentiation

Plotting the first derivative of the output signal is common practice in nuclear magnetic resonance and electron spin resonance work. Morrison (1954, 1963) has extended this technique to second derivatives in his efforts to optimize the results from ionization efficiency curves for the determination of ionization potentials. In 1954, Beynon et al., in a paper on "Derivative Mass Spectrometry", show that height and position of overlapping peaks can be determined more easily
and accurately from a record of the derivatives of the spectrum. Because differentiation is a linear operation, the relative amplitudes of the derivative spectra are unchanged from the original spectrum while the resolution is improved.

The authors show that the effective resolving power of the mass spectrometer can be controlled by the introduction of a new parameter, which is the amplitude of a small modulation applied to the accelerating voltage, and that the desired derivatives are proportional to the harmonics of the modulation frequency, if the modulation amplitude is kept within certain limits. The derivative spectra can be obtained by replacing the conventional dc amplifier by a narrow band ac amplifier.

The method is experimentally similar to the procedure for centering the ion beam on the collector slit, as used by Duckworth and his associates and described by Kerr et al. (1959). The accelerating voltage is modulated with a small 60-cycle sinusoidal voltage without disturbing the stability of the supply. The ion beam is thus swept back and forth across the collector slit, setting up a distinctive pattern on the oscilloscope screen. Equidistant maxima of this pattern are used as the criterion for a correctly centered beam. Kerr does not relate the method to derivatives of the spectrum, as Beynon does.

The resolution improvement of the method can be understood from some elementary considerations: the first derivative of a peak will give a positive and negative peak-pair which, for a symmetric profile, is rotationally symmetric. The second derivative gives a negative extremum which is
often considerably sharper than the original peak. The simplest example is the Gaussian peak, \( y = \exp(-x^2/2s^2) \). At \( x = s \) its height has decreased to about 60\%, while its second derivative has already reached the zero level. Many spectra of physical interest have Gaussian peaks, or very nearly so, so that a double differentiation will sharpen them considerably. (For similar reasons Geophysicists for years have used second derivative potential field contours in prospecting.) The less fortunate aspect of the second derivative spectrum is also illustrated by this example: a single peak in the original spectrum will give rise to two side lobes for each peak which may complicate the interpretation of the derivative spectrum. This is one of the reasons why Beynon feels that derivative spectra cannot be used indiscriminately, and he explicitly limits the usefulness of the method to spectra obtained from mass spectrometers whose collector slit is not too wide.

For the fairly broad peak which is of special interest in this work, the derivative spectrum is of limited use. The first derivative is indeed very sharp, but its peaks are derived from those parts of the spectrum, where the positional error of the output of the servosystem is theoretically non-zero (Stacey, 1962; Russell and Stacey, 1965). Besides, even after filtering the original spectrum, the derivative spectrum has a relatively high noise level, which is worsened by the non-uniform scan rate which will be discussed later.
Peak positioning methods using the mid-chord (or the intersection with the signal of the best straight line through a number of mid-chord points at various heights of the peak) are really variants of the derivative spectrum methods and suffer from the same disadvantages (Parrish et al, 1964).

4.4 **Deconvolution**

It is well-known that the process of convolution of two time functions is equivalent to a multiplication of their Fourier transforms in the frequency domain. In the type of signal investigated, the two functions are a sum of impulses and the peak shape which is characteristic of the overall system response. Since the impulse transform is \( e^{-i\omega t_m} \), with \( t_m \) the position in time, the output signal will have as its spectrum

\[
Y(f) = \sum_m a_m e^{-i\omega t_m} \cdot P(f) \tag{4.1}
\]

If the peak shape or its transform, \( P(f) \), were exactly known, the input spectrum could be obtained by a simple division.

There are severe limitations for a practical application. Obviously the exponential sum will oscillate without damping. The periods of its terms are determined by the peak positions and are generally not harmonic. Even if the sum could be obtained numerically with a relatively high precision, the Fourier inversion will present convergence problems.

The other limitation arises from the fact that frequency and time correspond to very different forms of coding, and
small, obvious errors in either domain may correspond to a nearly nonsensical message in the other one (Blackman and Tukey, 1958, p.IX). The transform of the peak shape will rarely be known with the required accuracy. Lacking an a priori knowledge of the peak shape, the only estimate of its transform is the envelope of the spectrum of the output signal. Moreover, the division by the peak transform places undue emphasis on those regions of the spectrum in which the signal-to-noise ratio is lowest. To include this region in the inversion integral is quite meaningless. On the other hand, multiplying the spectrum now by a suitable function, say a square peak, before inverting, convolves the resulting comb with the transform of the square window. The dilemma is obvious: if the window is narrow enough to cut out the noise, the purpose of first dividing by the peak transform is defied, while too wide a window places undue emphasis on the noise contaminated range*. The method was suggested by Stokes (1948) and has again been considered by Dolby (1959), but does not seem to have been successfully employed.

An interesting approximate method was suggested by Bogert, Haley and Tukey (1963), but can only be used if one of the amplitudes, $a_m$, in equation (4.1) is considerably greater

---

* In simpler terms, to narrow the peaks requires the recovery of information over a broader frequency band. The higher frequency information may simply not be recoverable from the noise. The matched filter, which will be alluded to later, is one means of attempting the recovery of this required data.
than the others. Without loss of generality this could be assumed to be \( a_1 \). Then the logarithm of equation (4.1) is approximately given by

\[
\ln y(f) = \ln P(f) + \ln a_1 - i\omega t + \sum_{m=1}^{n} \frac{\alpha m}{a_1} e^{-i\omega (t_m-t)} \quad (4.3)
\]

The "frequency" of the cisoidal ripple depends on the peak positions in the original record, \( y(t) \), which could then be obtained by a further Fourier analysis. Bogert et al. prefer to work with the real power spectrum rather than the complex equation (4.3).

4.5 **Peak Locations by Derivative Mixing**

Although a Fourier transform method does not hold much promise of increasing the resolution of an overlapping spectrum, it points the way to another method which tries to circumvent the difficulties of different coding in the time and frequency domains, but still suffers from noise amplification. The method has been developed and used with some success for instance by Allan et al. (1964).

The transform of physical peak shapes is a decreasing function of frequency, and can be represented with reasonable accuracy by a power series. By the definition of the transformation the real part of any peak transform is an even function of frequency, while its imaginary part is odd. One can therefore write

\[
1/P(f) = \sum_{n=0}^{\infty} E_{2n} \omega^{2n} + iF_{2n+1} \omega^{2n+1} \quad (4.4)
\]
For a symmetric peak all $F_m$ are zero. Substitution of equation (4.4) into equation (4.1) and inversion of the Fourier transformation leads to

$$a(t) = \mathcal{F}^{-1}\left(\frac{Y(f)}{P(f)}\right)$$

$$= \mathcal{F}^{-1}\left(\sum_m a_m e^{-i\omega t_m}\right)$$

$$= \sum_{n=0}^{\infty} (-1)^n E_{2n} \frac{d^{2n}}{dt^{2n}} y(t)$$  \hspace{1em} (4.5)

for a symmetric peak, assuming that the interchange of the order of summation, differentiation and integration is a valid operation. To obtain the coefficients $E_m$ the reciprocal of a peak transform can be fitted in the least squares sense by a power series over that range of the spectrum which is considered useful. If a reasonable analytic expression for the shape is known the coefficients can be obtained directly from a Taylor expansion. If the series (4.5) converges strongly enough the spectrum may be considerably sharpened. For instance, a Gaussian peak shape, $y = \exp(-x^2/2s^2)$, will lead to

$$z(x) = \sum_{n=0}^{\infty} (-1)^n \frac{s^{2n}}{(2n)!4^n} \frac{d^{2n}}{dt^{2n}} y(t)$$  \hspace{1em} (4.6)

The message of Blackman, cited on page 64 is, of course, still valid for this method: small errors in the assumed peak shape may change the coefficients in the expansion of its transform by rather large amounts.

From a physical viewpoint, the method of mixed derivatives will hardly offer any advantages for the kind of peak obtained
from our mass spectrometer, because of the same objections raised in section 4.3 against the use of simple derivatives. Mathematically, this can be seen from the expansion of our peak in a form equivalent to (4.6). In equation (3.2) this writer suggests a semi-empirical form for the peaks shape of our instrument in terms of error functions. The Fourier transform of the sum appearing in equation (3.2) leads to a finite integral. However, the frequency spectrum of the peak is more easily found by remembering that the error function arose from a convolution of a Gaussian and a square peak. Accordingly, the spectrum will be the product of the transforms of the square window and the Gaussian, viz.

$$P(f) = K \frac{\sin(\omega_c/2)}{\omega_c/2} \exp\left(-\omega^2/2(r\omega_c/2)^2\right)$$  

(4.7)

The constant $K$ is of no concern since we are interested in relative amplitudes only. As predicted for a symmetric peak shape the reciprocal of equation (4.7) can again be expanded in even powers of frequency, given to terms of fourth order by

$$K/P(f) = 1 + \frac{1+3n^2}{6} (\frac{\omega_c}{2})^2 \omega^2 + \frac{7+39n^2+45n^4}{360} (\frac{\omega_c}{2})^4 \omega^4$$  

(4.8)

The term $\omega_c/2$ is now the half width of the peak, equivalent to $s$ in equation (4.6). The coefficients are very sensitive to changes in $r$ and $\omega_c$. For a typical $r = 0.2$, one obtains approximately
\[ z(t) = y(t) - \frac{1}{6} (\frac{w_c}{2})^2 \frac{d^2 y(t)}{dt^2} + \frac{8}{360} (\frac{w_c}{2})^2 \frac{d^4 y(t)}{dt^4} \] (4.8)

Compared with equation (4.6) the series (4.8) converges slowly. While the second term is about the same as in (4.6) the third term is already eight times as large and it becomes necessary to include more of the noisy higher derivatives. Derivative mixing alone does, therefore, not hold much promise for our purposes. A more suitable method based on integration rather than on differentiation is described in the following section.

4.6 Peak positions by Integration or Cross Correlation.

With one exception, all peak positioning methods discussed above involve the calculation of numerical derivatives, or its equivalent. However, presented with a choice between a derivative and an integral method of otherwise equal merits the integral method will usually be favoured. The present writer has developed such an integral method for his specific purpose, which does not seem to have been used in mass spectrometry before. The method is the numerical equivalent of the densitometer described by Franks et al. (1964) which has been used by him for exact and consistent positioning of lines on photographic records. In this instrument a photocell with a slit aperture is moved along the film, which integrates the light transmitted by the film over the width of the slit. In mathematical terms this is simply the crosscorrelation of the recorded spectrum and a square peak. For equidistant observations this is
\[ c_n = \sum_{m=-L/2}^{+L/2} y_{n+m} \]  

(4.10)

where \( y \) is the signal, and \( L \) is the half width of the slit in units of the sampling interval. In physical terms, the square peak is comparable to a moving collector slit and the maxima of the crosscorrelation will occur when the maximum total current of any single ion group is collected. Small effects of short period noise, of the asymmetry of the beam, or of instabilities of the measuring system are averaged out, while in the method of peak positioning by differentiation their effects are accentuated. The peak position is then defined as the maximum of the parabola drawn through the three highest points.

The choice of the width of the numerical slit is not very critical, but underlies some obvious restrictions. If the square peak is too narrow it will be nothing but another smoothing of the spectrum as has already been applied before the reduction (cf. Chapter 2). If it becomes too wide, any one range of integration may extend over part of two adjacent masses, and the peaks in the correlation will run into one another. The actual choice has been made on the basis of some numerical experiments; the results obtained for a typical spectrum are illustrated in Figure 4.1. The width of the square peak, with which the spectrum was crosscorrelated is plotted as ordinate against the maxima of the crosscorrelation, obtained from the parabolic interpolation between three points. The peak
Figure 4-1 Peak positions by crosscorrelation.

The lines pass through all experimental points.
tops have a width of about 0.2 mass separations, therefore a valid peak position would not be expected for a peak width of less than this. Indeed, the positions obtained from such narrow correlations tend to drift by as much as 0.09 mass separations for the minor 248, 250 and 255 peaks, due to sloping tops. Note, that the horizontal scale is 0.2 mass separations per inch, and is discontinuous. For widths of about 0.3 to 0.4 the positions of the major peaks remain stationary within approximately one thousandth of one unit, while at correlation peak widths greater than 0.45 the effect of these major peaks on their small neighbours begins to be felt. Clearly, this integral method will not be desirable for spectra with strongly overlapping peaks but it works exceedingly well for the spectra of interest in this thesis. An extension of this method is suggested in section 4.7, which should be applicable to spectra with more overlap than ours.

The relation between the filtered signal and the cross-correlation is shown in Figure 4.2. The upper row shows the upper 10 percent of the broad and asymmetric peak tops of masses 249, and 251 to 253. Below them are the corresponding regions of the crosscorrelation. The asymmetry has disappeared almost completely, and the parabolic interpolation between the highest three points is well justified. The maxima will not in general coincide with the maxima of the original peaks, even after filtering, but rather be centered on the total area under each peak. The differences of the maxima of the original
Figure 4-2 Comparison of filtered peaks and crosscorrelation.

a: filtered peaks (cf. Section 2.4.5).

b: crosscorrelation with square peak. 0.4 mass separations wide.
data and the values calculated from the filtered spectrum for the positions determined from the crosscorrelation by interpolation is no worse than about 0.03 percent of the peak height.

4.7 Partial Deconvolution

The method described in the previous section works satisfactorily for the automatic reduction of mass spectra obtained in this laboratory. However, only the peak tops are sharpened, while the resolution of the spectrum is not improved. A method is suggested below, which is a combination of the methods of sections 4.2, 4.5 and 4.6.

To obtain the sharpest possible spectrum for a given beam width, the collector slit width should be made equal to the width of the beam. With a square beam cross section, triangular peaks would be obtained whose base is twice the beam width. If the collector slit width is further decreased, the peak base will still be diminished, but the tops will again widen. Therefore, the best combination of a sharp and well-resolved spectrum is achieved by a slit which has the same effective width as the beam. A similar problem has been treated by Bogert (1962), who was interested in substituting a more desirable frequency response for the actual response of a seismometer. The approach is essentially similar to the ones described in sections 4.4 and 4.5 of this thesis.

If the beam is given by \( g(x) \), the output signal is

\[
y(x) = g(x) \ast D_0(-x),
\]
where \( D_0 \) is the boxcar function (Blackman and Tukey, 1958, p.68) or square window. A substitution of a narrow window, \( W(f)_{\text{desired}} \), for the wider \( D_0 \), still leads to a division in the frequency domain. We now have

\[
z(x) = \mathcal{F}^{-1}(Y(f) \cdot W(f)_{\text{desired}}/D_0)
\]

As in section 4.5, \( 1/D_0 \) could be written as a power series, leading to

\[
z(x) = \sum_{n=0}^{\infty} (-1)^n E_{2n} \frac{d^{2n}}{dt^{2n}} (y(x) \ast w(x))
\]

where the actual window, \( D_0 \), has been assumed to be symmetric, and the \( E_m \) are determined by the transform of this window. Unfortunately, \( D_0(f) \) is the square collector slit; apart from some possible edge effects, its Fourier transform is proportional to a diffraction pattern, and an expansion in inverse powers of frequency does not converge rapidly. Equation (4.11) describes a consecutive application of the integral method of peak positioning discussed in section 4.6, followed by resolution enhancement by derivative mixing. The disadvantages of either method are partly eliminated by the other.

4.8 Conclusions

Of the methods of peak positioning that have been discussed, one group is designed to increase the resolution of a signal with strong overlap. Basically these methods all suffer from the same effect, namely a strong noise amplification. In many cases however, it will be well worth while to obtain
a noisy but resolved spectrum. For a record with rather broad peaks like ours these methods alone are less useful. Other methods discussed included a correlation technique which is now employed by this writer in the automatic reduction of lead spectra. The technique is the numerical equivalent of the densitometer method of peak positioning described in the literature. A combination of a correlation technique with a method of the first group is suggested, which should magnify the effective resolution of the mass spectrometer in this laboratory several times.
CHAPTER 5
PEAK AMPLITUDES

5.1 Introduction

The third set of parameters which the experimenter wishes to determine from signals of the type discussed in this thesis represents the pure peak amplitudes, free from contributions from their neighbours. The precise determination of peak height ratios is, of course, the main goal of isotope abundance mass spectrometry with which our laboratory is concerned. While the problem is basically still a deconvolution, the emphasis is now on the precision of the calculated peak amplitudes. This will modify the approach, and influence the choice of a technique, although the methods used are similar to the ones discussed in the last chapter. For instance, the method of derivative mixing, discussed in Chapter 4, not only leads to a sharper definition of the peak positions, but the merging signal should be proportional to the deconvolved record. However, in Chapter 4 the use of derivatives was rejected because it accentuated the noise of the signal. The same objection must now be made to the use of techniques involving numerical derivatives of the digitized record.

The measure of one particular peak amplitude can be obtained in two distinctly different ways. Either the observed value at the peak center or, alternatively, the total area under the peak can be used. In both cases the values obtained
will include the effects of peak overlap which must be removed. If the peak shape is known, this correction for the case of a height measurement is achieved by the solution of a system of simultaneous linear algebraic equations. The columns of the matrix represent the known peak shape, and the coefficient vector are the peak heights. In the case of an area measurement the overlap is removed in a similar fashion as we shall see in a later section.

To obtain a high precision the integration over the total area under a peak appears to be the superior method because short period noise in the amplitude of the signal is averaged out. However, the area measurement involves two dimensions, and the precision of the final result will critically depend on the precision of measurement of both.

The use of an instantaneous peak reading on the other hand does not provide any means to eliminate the effects of high frequency noise (cf. Figure 2.3), and is therefore of little use and rarely employed. When recording by hand, the operator will average by eye the output over a short time interval; in the reduction of the digitized record some filter will be applied (cf. Chapter 2), corresponding to an integration over a limited range around the peak center. The precision of the average obtained for the peak height will increase with the number of points included in it. Both suggested techniques are thus seen to involve an integration which is clearly preferable to the use of differentials. The main difference
between the two methods is the range over which the integration extends. The choice of the method of measuring peak heights for the reduction of the digitized lead spectra must therefore be based on a comparison of the noise amplitude remaining in the record after filtering with the irregularities in the abscissa of the record which contribute directly to variations in peak area.

5.2 The Choice for Our Record

In the design of our mass spectrometer no attempt has been made to obtain a linear scan rate. In Chapter 3 we have indicated that the scan rate was non-linear in time and suggested that a few terms of a power series relation would correct this for the purposes of Chapter 3. However, small irregular variations of the scan rate cannot be accommodated in this way and will lead to similar variations in peak widths. This noise is of the order of one to three percent, which is invisible on the chart record, but does show quite markedly in a calculation of peak heights based on area measurement. As an illustration, the peak widths obtained from a typical pair of down and upmass scans are shown in Figure 5.1. It shows clearly that the noise in the scan rate is greater by about.

* The peak width could be measured in different ways. For present purposes, the widths are best measured by the ratio of peak area over height. Area is defined by integration over a range of the spectrum slightly wider than the peak. If the variations in this ratio are much greater than the variations observed in the peak heights they must be caused by irregularities in the widths. The plotted points have been calculated in this way. Tests with the first derivative spectrum show similar results.
Figure 5-1 Fluctuations in the variation of peakwidths of one scan pair.
an order of magnitude than the tolerable errors (a few tenths of one percent) in the measurement of single peak heights. For the measurement of abundances with a precision greater than about one percent the area sensitive method is therefore useless and peak heights must be employed until the noise associated with the scan has been removed.

6.3 Abundance Ratios from Peak Heights

In Chapter 2 we showed that the numerical filter applied to the record before further reduction is equivalent to a weighted average over seven observations. At a scan rate of 2.5 masses per minute and a sampling rate of two per second, this is less than the width of the narrowest peak tops. The values of this smoothed record are therefore not affected by variations in peak widths, and the best readings for the peak heights that can be obtained are the values which are interpolated between the data points for the peak locations previously determined by the technique described in Chapter 4. If the height of the peak tails is known (cf. Chapter 3), an equation can be set up for the amplitude at each peak position in the record, expressing the observation as a linear combination of all other peaks. This system of equations is the discrete analogue of the convolution integral. In the case of the trimethyllead spectrum the solution of the simultaneous equations is relatively trivial because the off-diagonal terms of the coefficient matrix are so small relative to the diagonal terms of unity that already the second order terms in a power
series expansion of the inversion matrix are considerably smaller than the uncertainty in the first order terms. Since the determinant of the superposition matrix is the same for all peaks, and since only abundance ratios are desired, the determinant is ignored in the calculation.

If the magnitude of the tailing effect is not known the number of equations representing the convolution integral must in general be increased. For instance, some or all minima between the peaks may be used. The resulting equations may then become non-linear, leading to an iterative determination of the required peak parameters. Because the tail heights at the distances of neighbouring peaks are only small fractions of one percent in our records, one step in this iteration is sufficient, using the initial estimates of the peak heights. In this way the calculation of the tailing can be completely separated from the calculation of peak heights (cf. Chapter 3).

5.4 An Analog Method

If the overlap of the peaks in the spectrum is large, the inversion of the convolution matrix and the calculation of pressure factors becomes more difficult. Particularly for such cases an analog computer, such as the resolving power multiplier built and described by Kendall (1961, 1962) can be a valuable tool. Using comparatively simple circuitry, the instrument attempts to match an artificial record to the output of a spectrometer.
Kendall presumes a knowledge of the current pattern due to a single ion beam, i.e. the peak shape, and generates an analog peak in a discrete form by applying a common voltage across a series of resistors which are mounted in parallel as arms of the wiper of a rotating switch. The admittances of these arms are proportional to the height of the peak shape at the points represented by the resistors. The output of the spectrometer is fed to the contacts of the rotating switch through a series of identical parallel RC combinations. The contacts are held at ground potential by feeding in a charge through the wiper arms, which is proportional but of opposite sign to the comparison voltage at the middle arm of the wiper, which represents the peak center. The wiper is continuously passed over the contact, with a period which is short compared to the time constant of the RC circuits and which is synchronized to the scan drive. The insertion of a diode prevents reversal of the current in the simulator, and is required for convergence. When the system has converged, all contacts are virtual grounds, and the currents flowing into them from the spectrometer output cancel those from the wiper arms. The voltage across the wiper then represents the deconvolved spectrum and is displayed on an oscilloscope.

In its simplest form only contacts for integral mass numbers are present. This, then, is a measurement independent of peak area. If some criterion for the validity of the preset peak shape is desired, more contacts are provided. For instance,
all halfmass points can be included in analogy with the procedure described in the previous section and Chapter 3. The best peak shape representation can then be judged from the apparent resolution of the oscilloscope display of the feedback voltage. As the number of contact arms is increased the measurement becomes more and more area sensitive.

Dynamically variable resistances in the wiper arms, which could be feedback controlled, are conceivable, but are not mentioned by Kendall.

5.5 Least Squares - A Measure of Area

In section 5.2 we decided that for the present an area sensitive method of reducing our mass spectra is inferior to a height measurement. However, since the irregular scan rate can be corrected in various ways*, it is expected that area-sensitive measurements may not need to be excluded in the future. Then all recorded data points can be included in the analysis. Instead of the narrow averaging function applied to the data as in Chapter 2, the averaging process will be achieved by a matched filter, which is given by the crosscorrelation of the complete peak shape and the data points.

* Other mass spectrometers being constructed in the laboratory have different scan drives, and it is likely that they will be less noisy, though still non linear. In addition, a probe to measure the magnetic induction could be used to control the sampling rate so that \( B^2 \) rather than time is truly the independent variable.
For the purpose of this discussion we shall simplify the problem by assuming both peak positions and peak shape to be known. For the n-th observed point, \( y_n \), we can then write the equation

\[
\sum_{i} p_{ni} a_i = y_n \tag{5.1}
\]

where the sum is extended over all peaks, \( a_i \), which are possibly present in the record, and \( p_{ni} \) is the contribution of a unit peak at the i-th location to the n-th observation. This overdetermined system of equations is reduced to a square array by multiplying it with \( p_n \) and summing over all observations,

\[
\sum_{n,i} p_{nj} p_{ni} a_i = \sum_{n} p_{nj} y_n \tag{5.2}
\]

This approach is due to Gauss (cf. Jordan et al., 1961, vol.I, p.668) who has shown that the unknowns \( a_i \) obtained from a solution of the symmetric set of equations (5.2) are that set out of an infinity of possible solutions which has the smallest standard deviations. The only assumptions necessary are a symmetric error law for the observations and, in our special case, the same standard deviation for all observations. Equations (5.2) are identical to those obtained from equations (5.1) by an application of the widely used principle of least squares. The coefficient vectors of equations (5.2) are recognized as selected values of the crosscorrelation of the
peak with all data points and are therefore a measure of area*. (In the frequency domain the equivalent to this crosscorrelation is filtering with a "matched filter").

In the more general case the peak parameters are only approximately known, and must be determined along with the best peak heights. If the analytic form for the peak suggested in Chapter 3 is used, the observational equations will be non-linear, and iterative procedures will be required. The methods are well-known, and shall not be discussed here. An excellent reference is the report by McWilliams et al. (1962) who have fitted series of Gaussian and Lorentzian peak shapes plus various forms of background signal to their data.

* This area dependence of a least squares analysis can be very simply demonstrated with a specific example. Let the spectrum consist of a single Gaussian peak, \( \exp(-x^2/r^2) \). Its width, \( r \), may be slightly different from the "correct" width \( s \), so that \( r = s(1+t) \). Attempting to fit this spectrum with a peak of correct width, \( \exp(-x^2/s^2) \), we wish to minimize

\[
\int (e^{-x^2/r^2} - ae^{-x^2/s^2})^2 \, dx = \min
\]

with respect to \( a \). (For convenience, the range of integration is infinite.) This leads, after differentiation and integration, to

\[
\frac{1}{(1/r^2 + 1/s^2)} - \frac{a}{2/s^2} = 0
\]

or

\[
a = \frac{2/s^2}{1/s^2+1/r^2} = 1 + t + 0(t^2)
\]

To first order terms the best fitting peak is therefore proportional to the area \((1+t)\) of the spectral peak.
Making use of the principle of least squares we are in a position to demonstrate the close analogy, but at the same time important difference between the two methods of peak height calculation discussed previously. Considering a very simple spectrum, made up of a single square peak of height one and width $1+e$, we wish to obtain the best fitting square peak (in the least squares sense) of width one. According to the sign of $e$ we have two distinct cases, which are illustrated in Figure 5.3. In case (a) the peak to be fitted is narrower than the spectral peak. The error sum (or

\[
\begin{align*}
\text{a:} & \quad \begin{array}{c}
\text{spectral peak too wide,} \\
\text{spectral peak too narrow.}
\end{array} \\
\text{b:} & \quad \begin{array}{c}
\text{spectral peak too wide,} \\
\text{spectral peak too narrow.}
\end{array}
\end{align*}
\]

Figure 5.3 Connection between width of averaging range and least squares peak heights. A peak of width one is fitted to a simple spectrum. cf. Text. a: spectral peak too wide, b: spectral peak too narrow.
integral) to be minimized is

\[ \int (y-ap)^2 \, dx = (1-a)^2 + e \]

Differentiation with respect to \(a\) and equating to zero gives

\[ a = 1 \]

i.e. the best least squares height equals the true height, if the chosen peak shape is narrower than the actual peaks in the spectrum.

In the opposite case we have

\[ \int (y-ap)^2 \, dx = (1-a)^2(1-e) + a^2e \]

and \[ a = 1 - e \]

i.e. the best least squares height is proportional to the peak area if the chosen peak shape is wider than the actual peaks in the spectrum.

For the square peak, the transition between the two cases is discontinuous. For the Gaussian (footnote on page 82) the transition is smooth but still the result is area dependent when \( s \gg r \) and area independent when \( s \ll r \). This relationship is generally true and it is one of the most fundamental considerations in the reduction of digitized mass spectra.

5.6.1 Precision of Automatic Reduction. It is not easy to evaluate the precision of the performance of the automated reduction system and to compare it with manual recording and calculations. The main cause of difficulty is that the precision
of measurement varies from one run to the next. Small variations in running conditions influence the standard deviations of the measurements more than the particular method of readout and reduction does. Unfortunately it is not possible to digitize the output and simultaneously record by the dial method.

Two tests seem to offer opportunity for an evaluation of the relative merits of automation versus hand reduction. The first is the comparison between the results obtained from a digitized analysis and a carefully done hand reduction of the same analysis from chart measurements. This has been done, and in order to obtain an estimate of the objectivity of the analyst, the hand reduction has been repeated independently by two persons. The results are listed in Table 5.1. The standard deviations for a single pair of scans from the overall average for each analysis is given for the four major peaks of masses 249, 251, 252 and 253. In columns five to nine the ratios of the standard deviations to the corresponding values of the standard automatic reduction of the same analysis are given. To show the effect of the adjustment of the base lines described in Chapter 2, the two digitized analyses were reduced both with and without the adjustment of base lines. The values given for the hand reduction should therefore first be compared with the completely equivalent values in part B of the Table. Although the occasional entry in part A is slightly lower than that in part B, the overall averages indicate a distinct superiority of machine over hand reduction,
Table 5-1 Standard deviations (\(\sqrt{\frac{\sum(a-\bar{a})^2}{(n-1)}}\)) of handreduction and machine reduction.

A: Handreduction by 2 persons (1,2); two runs (I,II).
B: The same analyses using average bases.
C: As above with least-squares-adjusted bases.

<table>
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<tr>
<th>Description</th>
<th>Standard deviation of one pair of mass (in .01%)</th>
<th>Ratio</th>
</tr>
</thead>
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<td></td>
<td>reduction method</td>
<td>Run</td>
</tr>
<tr>
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<td>NO</td>
</tr>
<tr>
<td>Hand, 2</td>
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<td>NO</td>
</tr>
<tr>
<td>Hand, 1</td>
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<tr>
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<tr>
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<td>NO</td>
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<tr>
<td>Average</td>
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<td></td>
</tr>
<tr>
<td>Auto-reduction</td>
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<tr>
<td>Auto-reduction</td>
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<td>YES</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
and of the base-adjusted values over those without this adjustment.

The second test demonstrating the precision of the automatic technique is a comparison of the standard deviations of the mean trimethyllead peak heights \( \sqrt{\frac{(a_i - \bar{a})^2}{n(n-1)}} \) obtained in the course of a typical intercomparison loop, with corresponding values reported by Ostic (1963, p. 30, 31).*

Table 5-3-a lists our values for seven analyses giving both the absolute and the percentage mean of the standard deviations and the number of pairs in each analysis; part (b) lists Ostic's values. Figure 5-4 is a photo-copy of a computer produced final report of isotopic abundances of one analysis.

These comparisons of the two recording and reduction techniques demonstrate that, as well as being more efficient, the automatic procedures offer a slight superiority in precision.

5.6.2 Measurement of the Mass 249 Peak. The machine methods described in the preceding section were closely similar to the method used in hand reduction so that a valid comparison of the methods could be made. For instance, in reading the dial, the minimum readings (averaged by eye over a short interval) adjacent to the mass 249 peak were recorded and their average used as reference for the measurement of the

* The analyses of this writer were made when the mass spectrometer performance was thought to be less than satisfactory; this comparison of absolute standard deviations therefore, if anything, discriminates against the automatic procedure.
Table 5-3  Typical standard deviations of mean peak heights.

A comparison of the precision obtained between:
(a) automatic reduction by the writer,
(b) hand recording and reduction (from Ostic, 1963, p.31)

<table>
<thead>
<tr>
<th>MASS NO. OF PAIRS</th>
<th>249</th>
<th>251</th>
<th>252</th>
<th>253</th>
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<td>.00027</td>
<td>.0036</td>
<td>.0030</td>
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<td>7</td>
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</tr>
<tr>
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<td>.00021</td>
<td>.0020</td>
<td>.0020</td>
<td>.0023</td>
</tr>
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<td>6</td>
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<td>.0016</td>
<td>.0024</td>
<td>.0026</td>
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<td>7</td>
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<td>.0017</td>
<td>.0020</td>
<td>.0028</td>
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<tr>
<td>MEAN VALUES</td>
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<td>.0024</td>
<td>.0037</td>
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<td>PERCENT OF PEAK</td>
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<td>.011</td>
<td>.007</td>
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b:

<table>
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<tr>
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<th>.0047</th>
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<td>.0028</td>
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<td>.0022</td>
<td>.0046</td>
<td></td>
</tr>
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<td>.0028</td>
<td>.0029</td>
<td>.0044</td>
<td></td>
</tr>
<tr>
<td>.0003</td>
<td>.0013</td>
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</tr>
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<td>.0022</td>
<td>.0051</td>
<td></td>
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<td>.0004</td>
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<td>.0050</td>
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<td>MEAN VALUES</td>
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<td>.0024</td>
<td>.0043</td>
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<tr>
<td>PERCENT OF PEAK</td>
<td>.026</td>
<td>.012</td>
<td>.011</td>
<td>.008</td>
</tr>
</tbody>
</table>
LEAD TRIMETHYL REDUCTION WITH (3) ORDER INTERPOLATION

POLYNOMIAL COEFFICIENTS

\[
\begin{array}{c|cccccccccccc}
1 & 2465. & 401. & 39734. & 40000. & .89259. & 2961. & 0.010 & 0.010 & 0.010 & 0.010 & 0.010 & 0.010 & 0.010 \\
2470. & 398. & 39775. & 40044. & .89359. & 2965. & 1.402 & 0.229 & 22.716 & 22.858 & 51.100 & 1.696 \\
2466. & 399. & 39721. & 35982. & .89178. & 2958. & 1.402 & 0.228 & 22.715 & 22.864 & 51.097 & 1.695 \\
2470. & 396. & 39777. & 40071. & .89406. & 2967. & 1.401 & 0.229 & 22.716 & 22.859 & 51.100 & 1.694 \\
2465. & 401. & 39789. & 35952. & .89159. & 2954. & 1.402 & 0.229 & 22.714 & 22.857 & 51.104 & 1.695 \\
2470. & 399. & 39771. & 40064. & .89390. & 2964. & 1.402 & 0.229 & 22.716 & 22.859 & 51.100 & 1.694 \\
2465. & 399. & 39751. & 40037. & .89355. & 2966. & 1.402 & 0.229 & 22.714 & 22.857 & 51.104 & 1.695 \\
2465. & 399. & 39727. & 40013. & .89260. & 2960. & 1.402 & 0.228 & 22.713 & 22.861 & 51.102 & 1.695 \\
2471. & 396. & 39771. & 40036. & .89358. & 2964. & 1.402 & 0.228 & 22.713 & 22.861 & 51.102 & 1.695 \\
\end{array}
\]

Fig. 5-4 Photocopy of a computer-produced final report sheet for one sample.
249 peak. In machine reduction the same was done, but the averaging process and the interpolation achieved in a more consistent fashion. After demonstrating the general superiority of the machine procedure we now wish to investigate the merit of obtaining the important 249 peak in the fashion described above.

The measurement of the mass 249 peak is of special importance because all quantitative interpretations depend on the ratio to it of the three heavier stable isotopes. In the past, when the 249 peak was measured as described above, a correction was added to its measured height which was intended to account for the rise of the background near that peak due to its own tail. Lacking detailed knowledge of the peak, an estimate for the tail height at about one half mass separation from the peak center was used, (usually twice the one-mass coefficient). A quite reliable estimate of the sum of the up and downmass halfmass tail height can be obtained from the minimum value between the two peaks of mass 251 and 252. It is observed to be about 0.3 percent per microtorr of pressure. However, the minima adjacent to the 249 peak do not occur at the one halfmass point but will be shifted further towards the weak neighbours of masses 248 and 250. This is an example of a case where the hand reduction did not provide sufficient information about the peak shape.

The halfmass correction is thus seen to be insecure, and we now present evidence that the mass 249 peak is preferably measured in the same way as the other peaks from the base lines which are established at either end of the scan. This leads to
an improvement in the standard deviations of the mass 249 measurements. In Table 5.2 we exhibit the standard deviations of the 249 peaks, placing together the values of corresponding runs, and the average of each group. In the few cases where measurement from the base leads to higher values, the difference is very small. It seems worth pointing out that one of the runs included in Table 5.2 was made while the pressure dropped from 2. to 0.9 microtorr and the peaks became so small that halfway through the run the 249 peak had to be measured on the highest sensitivity range; on this range the high frequency noise is about one percent of the height of the 249 peak. The standard deviation for this pair does not in the least appear to reflect the very high noise level. On the basis of this strong evidence, and because of the difficulties of the halfmass correction, the writer recommends the future use of an outside base for the measurement of the mass 249 peak.

5.6.3 Example. The isotope ratios obtained for a sample depend strongly on the precision of the measurement of the non-radiogenic isotope of mass 204 because it is used as reference for the other isotopes of masses 206 to 208. However, the abundance of lead-204 is less than ten percent of any of the other abundances. An error in its evaluation will result in a corresponding error in the calculation of all isotope ratios. The error in the measurement of mass 249, corresponding to lead-204, may be partly of a random nature, but if two samples are not compared at identical pressures, a strong pressure bias
Table 5-2 Standard deviation of $^{249}$-peak when measured from different background levels. ($\sqrt{\frac{1}{n-1}} \cdot (\bar{a}-a)^2$) in 0.01%.

<table>
<thead>
<tr>
<th>Measured from</th>
<th>Interpolated background</th>
<th>Ratio</th>
</tr>
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<tbody>
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<td>16</td>
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</tr>
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<td>24</td>
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</tr>
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</tr>
</tbody>
</table>

* This set measured on shunt 1.
would be introduced by the application of incorrect tailing corrections. Although in practice it is attempted to hold pressures of different samples as similar as possible, pressure differences of the order of one microtorr occur.

If the peak of mass 249 is measured from the baseline, the important corrections which have to be applied are the tail height at two mass units downmass and, depending on tail length, the three and four mass tail heights. In Chapter 3 the tail height at two mass units downmass was seen to be about 0.02 percent per microtorr. The corresponding correction of mass 249 amounts to about 0.3 percent per microtorr, due principally to the mass 251 peak. The uncertainty in the one mass correction was reported to be about 0.02 percent per microtorr. Because the peaks affected by this correction are all of the same magnitude, the uncertainty in the one-mass correction is negligible with respect to the uncertainties in the final isotope ratios due to the corrections applied to mass 249. In the following example we shall therefore only consider the effects of the correction applied to mass 249, using the average value for the other corrections as calculated by the standard program, using equation (3.3).

To demonstrate the precision of the automated reduction system, and the effects of slight variations in the length of the downmass tail, repeated computations were made for a series of analyses forming an intercomparison loop (cf. Appendix I for detailed description of the looping technique).

* This is not true for mass 254, but it is only used as a correction for the final isotope ratios, hence an error in its determination is a second order effect.
The loop contains two intercomparisons in which the pressure of the second sample was appreciably higher than the first. If the pressure corrections for the 249 peak are applied incorrectly, the error in these two comparisons will not cancel. The loop closure error of the three isotope ratios 206/204, 207/204 and 208/204 will then be of the same sign, while for an unbiased correction the closure errors should scatter around zero.

Equation (3.5) becomes almost linear close to the zero of the tail, and for an approximate tail length of 3.5 mass units the tail height at three mass units will be about one third of the height at two mass units. The loop closure calculation was therefore done for variations of the third downmass factor from 30 to 50 % of the second downmass factor. Table 5.4 shows the results of these calculations. The loop closure error is indeed of opposite sign at either end of this range, and the same for all isotope ratios. The sum of squared loop closure errors could be chosen as a criterion for the best third mass correction. Its minimum occurs at about one-third of the second downmass factor, corresponding to a tail length of less than 4 units if equation (3.4) is used. Figure 5-5 shows the composition of samples 493 and 436 relative to the laboratory standard (Broken Hill No. 1) calculated for the different third mass factors. In accord with the standard deviation of the differences in Table 5.4 it is seen that the differences in isotopic composition of the two samples cannot be caused by faulty pressure corrections.
Figure 5-3 Compositions of samples 436 and 493 (Brittania). Given with respect to laboratory standard (Broken Hill No.1). Standard errors for $D_3 = 0.4D_2$ are indicated by ellipses.
Table 5.4 Loop closure calculations with different assumptions for the third downmass pressure correction.

\( y_d, D_3 \) are the tail heights at 2, 3 units down mass

\[ D_3 = 0.2 y_d \]

<table>
<thead>
<tr>
<th>Isotope ratio Sample No.</th>
<th>206/204</th>
<th>207/204</th>
<th>206/204</th>
</tr>
</thead>
<tbody>
<tr>
<td>436</td>
<td>18.564</td>
<td>15.634</td>
<td>38.326</td>
</tr>
<tr>
<td>493</td>
<td>18.532</td>
<td>15.604</td>
<td>38.261</td>
</tr>
<tr>
<td>Difference</td>
<td>0.033</td>
<td>0.030</td>
<td>0.064</td>
</tr>
<tr>
<td>Adjusted difference</td>
<td>0.0235</td>
<td>0.0229</td>
<td>0.0627</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.017</td>
<td>0.014</td>
<td>0.003</td>
</tr>
<tr>
<td>493</td>
<td>18.533</td>
<td>15.599</td>
<td>38.223</td>
</tr>
<tr>
<td>l</td>
<td>16.055</td>
<td>15.448</td>
<td>35.897</td>
</tr>
<tr>
<td>Difference</td>
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<td>0.151</td>
<td>2.326</td>
</tr>
<tr>
<td>Adjusted difference</td>
<td>2.4699</td>
<td>0.1444</td>
<td>2.3242</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.016</td>
<td>0.014</td>
<td>0.0031</td>
</tr>
<tr>
<td>l</td>
<td>16.063</td>
<td>15.461</td>
<td>35.887</td>
</tr>
<tr>
<td>436</td>
<td>18.543</td>
<td>15.616</td>
<td>38.271</td>
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<td>-0.155</td>
<td>-2.384</td>
</tr>
<tr>
<td>Adjusted difference</td>
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<td>-0.1673</td>
<td>-2.3869</td>
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<tr>
<td>Standard deviation</td>
<td>0.020</td>
<td>0.018</td>
<td>0.004</td>
</tr>
<tr>
<td>Loop closure error</td>
<td>0.0308</td>
<td>0.0268</td>
<td>0.0062</td>
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</tbody>
</table>
Table 5-4 Continued.

\( \text{D}_3 = .3 \ y_d \)

<table>
<thead>
<tr>
<th>Isotope ratio sample No.</th>
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<th>207/204</th>
<th>208/204</th>
</tr>
</thead>
<tbody>
<tr>
<td>436</td>
<td>18.573</td>
<td>15.641</td>
<td>38.343</td>
</tr>
<tr>
<td>493</td>
<td>18.546</td>
<td>15.616</td>
<td>38.292</td>
</tr>
<tr>
<td>Difference</td>
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<td>.025</td>
<td>.051</td>
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<tr>
<td>Adjusted difference</td>
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<td>.0200</td>
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</tr>
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<td>Standard deviation</td>
<td>.011</td>
<td>.009</td>
<td>.009</td>
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<tr>
<td>493</td>
<td>18.540</td>
<td>15.605</td>
<td>38.236</td>
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<td>1</td>
<td>16.064</td>
<td>15.457</td>
<td>35.919</td>
</tr>
<tr>
<td>Difference</td>
<td>2.475</td>
<td>.147</td>
<td>2.317</td>
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<tr>
<td>Adjusted difference</td>
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<td>Standard deviation</td>
<td>.011</td>
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<td>.008</td>
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<td>1</td>
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<td>15.468</td>
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<td>436</td>
<td>18.552</td>
<td>15.623</td>
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<td>-2.385</td>
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<td>.018</td>
<td>-.016</td>
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Table 5-4  Continued.

\[ D_3 = 0.4 y_d \]

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<th>208/204</th>
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<td>.020</td>
<td>.038</td>
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<tr>
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<td>493</td>
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<td>18.546</td>
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<td>1</td>
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<td>Standard deviation</td>
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<td>.004</td>
<td>.020</td>
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<td>1</td>
<td>1</td>
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<td>15.630</td>
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<tr>
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<td>.006</td>
<td>.026</td>
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<tr>
<td>Loop closure error</td>
<td></td>
<td>.0096</td>
<td>.0083</td>
<td>-.0387</td>
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</table>
Table 5-4  Continued.

\[ D_3 = .5 y_d \]

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<tr>
<th>Isotope ratio</th>
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<th>206/204</th>
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<th>208/204</th>
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<tbody>
<tr>
<td></td>
<td>436</td>
<td>18.589</td>
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<td>15.641</td>
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</tr>
<tr>
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<td></td>
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<td>.014</td>
<td>.024</td>
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<tr>
<td>Adjusted difference</td>
<td></td>
<td>.0136</td>
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<td>.0413</td>
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<tr>
<td>Standard deviation</td>
<td></td>
<td>.0006</td>
<td>.0005</td>
<td>.032</td>
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<tr>
<td></td>
<td>493</td>
<td>18.553</td>
<td>15.616</td>
<td>38.264</td>
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<td>1</td>
<td>16.084</td>
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<td>35.964</td>
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<td>2.469</td>
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<td>2.301</td>
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<tr>
<td>Adjusted difference</td>
<td></td>
<td>2.4690</td>
<td>.1399</td>
<td>2.3169</td>
</tr>
<tr>
<td>Standard deviation</td>
<td></td>
<td>.0006</td>
<td>.0005</td>
<td>.032</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>16.085</td>
<td>15.482</td>
<td>35.936</td>
</tr>
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<td></td>
<td>436</td>
<td>18.568</td>
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<td>38.322</td>
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<td>-2.483</td>
<td>-.155</td>
<td>-2.386</td>
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<tr>
<td>Adjusted difference</td>
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<td>-.1544</td>
<td>-2.3581</td>
</tr>
<tr>
<td>Standard deviation</td>
<td></td>
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<td>.0006</td>
<td>.0415</td>
</tr>
<tr>
<td>Loop closure error</td>
<td></td>
<td>-.0011</td>
<td>-.0009</td>
<td>-.0612</td>
</tr>
</tbody>
</table>
Although many more complete loops will have to be analyzed in order to give the $D_3$ factor a good statistical backing, Figure 5.5 shows that near the optimum value of $D_3$ of about 0.3$\nu_d$ the isotope ratios change but little. The value for the third mass correction in the down mass direction can be taken, with little error, as one-third the second mass correction. Of course both these pressure scattering factors are zero in the upmass direction.

6.7 Conclusions

The methods considered for a precise determination of peak heights all depend on an averaging process in order to eliminate the effect of short term fluctuations of the signal. If the uncertainties in the abscissa are negligible with respect to noise in the signal ordinate, the best estimate of the peak heights is obtained from a crosscorrelation of the ideal peak shape and the record. This corresponds to a minimization of the squared differences between an artificial and the actual record. If the correct peak shape is not accurately known its parameters can be obtained from a more general least-squares analysis.

For our records it was shown that the noise in the abscissa is equivalent to about one to three percent of the peak widths. For peak height measurement of higher precision, as required in this laboratory, the averaging or crosscorrelation process must therefore be limited to a range narrow relative to the peak width.

Information about the peak tailing discussed in Chapter 4
has been applied to the inversion of the superposition matrix. In particular, the tail height at two mass units downmass \(y_d\), which is calculated by the present digital reduction program in conjunction with a tail length of about 3.5 mass units downmass, has been found to give the most consistent pressure correction for a complete loop of intercomparisons. The maximum standard deviation of the difference between samples was 0.08 percent.
CHAPTER 6
CONCLUSIONS

The purpose of the research culminating in this thesis has been twofold. Firstly, a general study was undertaken of the techniques which are available for the reduction of a special class of signals frequently encountered in experimental science. Secondly, the results of this study have been applied to the automatic reduction of the trimethyl group of the tetramethyllead spectrum, which is a member of the class of signals considered.

If a discrete set of similar physical phenomena is recorded by a measuring device, the signals due to the separate events will result in overlapping responses which constitute the spectrum. The example of special interest in this laboratory is the mass spectrum of a compound containing the four lead isotopes of masses 204, 206, 207 and 208. Although each mass has a sharply defined value, the various ion beams which are produced by electron bombardment and separated by the magnet have a finite extent and spread when observed during the measuring process. The ion current pattern which is finally recorded is continuous, and at each point of the spectrum contributions from several masses may overlap.

Often the signals due to each separate event are identical or very nearly so. The general process of their superposition can then be described mathematically by a convolution integral. In principle, the inversion of the
convolution appears to be easily effected by the use of the Fourier transformation if the peak shape is known. In practice, the presence of noise in the signal and the normally incomplete knowledge of the peak shape render the Fourier methods less useful.

Two sets of parameters are generally of particular interest to the experimenter. These are the positions with respect to the experimental variable of the physical events giving rise to the signal, and their relative intensities. The set of parameters defining the peak shape are only auxiliary variables needed to obtain the other sets.

One group of methods suggested in the literature for deconvolving a record are centered around the use of derivatives of the signal. In theory, these methods are closely related to the aforementioned Fourier techniques and also suffer from noise. In some reported cases the use of derivatives has facilitated information recovery.

Another group of methods can be derived from the principle of least squares or an equivalent approach. In the simplest case, when the peak shape and the positions are known, the measurement of amplitudes is based on a crosscorrelation. This is a convolution of the signal with the known wave or peak form which has been inverted in time. In terms of frequency content it is the matched filter for the signal. The integration involved in the crosscorrelation severely attenuates short period noise. Such a technique would be expected to be best adapted for a high precision measurement.
of peak amplitudes. It has been shown in this thesis that the choice of the crosscorrelation peak (or equivalently, the weighted averaging function) vitally affects the precision of the results of an amplitude measurement. As the averaging range is lengthened, the variations in the results due to fluctuations in the abscissa of the record become increasingly important. This fact does not appear to have been appreciated in mass spectrometry before.

The second phase of the work leading to this thesis was the development of a system for the automatic recording and reduction of the mass spectra which are obtained in this laboratory. The central portion of the peak shape in these spectra closely resembles the sum of two error functions. This may be evidence that the cross section of an ion beam of a single mass is approximately Gaussian. For the long peak tails which are observed a different expression must be used, representing the still not well-understood mechanism which is involved in spreading a small fraction of the beam as far as several mass units. The peak positions in our records are clearly recognized by a casual observer. However, to the electronic computer, the noise in both coordinates of small amplitude and high frequency presents some difficulties, which are overcome by the use of a correlation technique.

For the high precision measurement of peak amplitudes a method was selected which is relatively insensitive to short term fluctuations in the scan drive. This was necessary because the stability of the drive was shown to be of the
order of one to three percent. The precision of the automatic signal reduction was shown to be about 1.5 to 2 times better than the previously used method of hand recording and reducing. The main reason for the increase is the greater number of data collected and the more consistent and elaborate treatment of these data by the electronic computer.

The saving in the time required for the reduction of the data is considerable. Whereas previously in this laboratory a time delay of several days for the reduction of one set of data was about normal, the results can now be obtained within one day with the present computing facilities and the programs which have been prepared during this research.

Although the precision has not been increased several times as it was hoped initially the slight gain that was obtained seems to be real. This will have to be confirmed by many more analyses. Only little is gained by adjusting the average of the background readings at each end of the spectrum. The routine adjustment of bases has, however, given an interesting check on the statically determined attenuation factors: the average of 150 factors calculated from the observed base readings agrees to within about 0.02% with the statically measured values. In all cases the difference between the two values is smaller than one standard deviation of the average of the dynamically measured values.

It was shown that the mass 249 peak should be measured from a linear interpolation between the background on shunt-2 at the ends of the scan rather than from the minima at its
bases. The reason for the improved precision must be sought in the better averaging for the stationary values at the end of the scan. If measurement of the mass 249 peak from its sides is preferred for some reason, the halfmass correction factor should be critically reviewed. This writer believes that it is slightly less than twice the sum of the first upmass and downmass corrections.

The pressure corrections as presently calculated from equations (3.3) agree with the results of a least squares analysis only for the second upmass and downmass corrections. Although the least squares results are preferred it is realized that the least squares analysis is not easy to make on a routine basis. There is an obvious way around this difficulty. If the peak tails are expressed in a series of inverse powers of the distances from the peak center (or a fixed point near the center) the peak parameters appear linearly and the least squares analysis becomes simpler.

This writer believes that at present the precision of slightly better than 1 permill in the isotope measurements in this laboratory is not limited by the technique of data reduction. However, the application of the least squares method to the whole length of the spectrum should be reconsidered if the scan rate of a new instrument is found to be appreciably better than the present one.
BIBLIOGRAPHY


Kollar and Russell (1960) introduced in this laboratory an intercomparison technique for isotopic measurements of lead ratios. A number of upmass and downmass scans for a sample A is taken, then the second sample B is analysed, after which another analysis of sample A is made. The mass spectrometer settings and conditions for the three analyses are kept as identical as possible. The two analyses of sample A are averaged, with the underlying assumptions that small changes of conditions will average out, with the average ratios of sample A corresponding to a measurement taken simultaneously with sample B. On the other hand, a difference of the averages of the two A-runs (analyses) which is appreciably greater than the standard error of either mean will be regarded with some suspicion since a strictly linear drift of setup conditions over appreciable ranges seems hard to justify. In many cases however, it appears that the standard error of two combined runs of one sample is not appreciably greater than the greater one of the standard errors of a pair of one individual run. Sample B will then be intercompared with sample C on another day, running B-C-B in that order. A third intercomparison will involve samples C and A in the same manner. This constitutes a closed loop analogous to a level survey starting from a benchmark and closing on it. The sum of the measured differences between samples A-B-C-A should add up
to zero. In practice a small loop closure error will generally be obtained. It has been the adopted practice in this laboratory to spread this closure error evenly over the three isotopic differences regardless of the quality of the single intercomparisons. This corresponds to a minimum of the sum of squared adjustments in which unit weights are assigned to each intercomparison as will be shown below. This writer believes that the differences in standard errors of single intercomparisons are significant enough as to warrant a weighted distribution of the closure error. Moreover, a standard error of the adjusted differences between samples should be calculated for each comparison, as the differences themselves are often of the order of their standard deviation, and therefore their significance is not always immediately clear.

The computer-produced final report on an isotopic intercomparison has in the past included, besides other information, a standard error of a single peak as obtained for one pair (St. Err. = $\sqrt{\frac{1}{\sum (a_i - \bar{a})^2 / (n-1)}}$), and the final ratios normalized with respect to the 204-isotope. The opening and closing run of a day are often combined into one reported set of lead isotope ratios. If this is done, some judgment must be exercised with respect to the weighting of those runs. If a linear drift of the spectrometer is assumed to have occurred, the two runs must be given equal weight in order to obtain the most probable value of the isotope ratios at a time halfway between the opening and closing runs. If different
numbers of scans were used in each run, some scans should be rejected arbitrarily in one run, or pairs duplicated in the other, in order to obtain equal weighting in time. Equal weighting is still required if the standard errors of the runs are distinctly different. However, if one assumes the differences between the run averages to be of a random nature, which is justifiable if this difference is of the order of the standard error of either run, then the runs should be averaged inversely proportional to the standard error of their means. The usual procedure is to combine all pairs of opening and closing runs into one set of ratios and to calculate a standard error per pair for every mass peak for this combination. The peak ratios are then reduced to isotope ratios by applying corrections for the occurrence of $^{13}$C and the possible loss of one hydrogen atom. For purposes of error analysis the peak ratios and isotope ratios can be assumed to be the same, thus introducing an error of only a few percent in the calculated error. The variance of the calculated difference between two analyses is found by standard methods. The difference, for any mass is given by

$$d = \frac{P}{P_{249}} - \frac{P'}{P'_{249}}$$

(1)

The variance of $d$ is then given by

$$\text{var}(d) = (\frac{ad}{aq_1})^2 \times \text{var}(q_1)$$

(2)

(cf. eg. Fundamental Formulas of Physics, D.H. Menzel ed., Dover Public. N.Y. 1960, p.138.) where the $q_1$'s are the four
peaks appearing in (1). The errors in $q_1$ are assumed to be uncorrelated. Differentiation and substitution gives

$$\text{var}(d) = \frac{P^2}{P_{249}^2} \cdot \left( \frac{\text{var}(P)}{P^2} + \frac{\text{var}(P_{249})}{P_{249}^2} \right) + \frac{P'^2}{P_{249}^2} \cdot \left( \frac{\text{var}(P')}{P'^2} + \frac{\text{var}(P'_{249})}{P'_{249}^2} \right)$$

(3)

Let $e$ be the loop closure error, i.e. the sum of the observed differences for one mass. To find the most probable error of the differences one determines the minimum of the sum of the squared corrections, $d_i$, in a well known fashion, but under the constraint that the sum of the adjusted differences must be zero. Generally the method of undetermined multipliers is used to obtain a symmetric set of normal equations (Jordan, 1961), but for the given simple case the straightforward approach seems commendable and shall be given here.

With three observed differences and one constraint between the corrections, only two corrections, say $c_1$ and $c_2$, can be independently chosen, which then fix $c_3$ by

$$c_3 = -e - c_1 - c_2.$$  

(4)

Usually the differences will have different variances, and therefore should be weighted for maximum probability. The sum to be minimized is then

$$Q = w_1 c_1^2 + w_2 c_2^2 + w_3(e + c_1 + c_2)^2$$

(5)

and differentiation gives
The solutions of (6) can be written as

\[ c_1 = -e/(w_1 \sum_1^1 1/w_1) \]
\[ c_2 = -e/(w_2 \sum_1^1 1/w_1) \] (7)

with \( c_3 \) then being given by (4).

The variance of the corrections is obtained by the usual

\[ \text{var} = \sum_1^w c_i^2 / N-r \]

The number of observed differences is three, of independently fitted constants two. The variance of an observation of unit weight is therefore equal to the weighted sum of squared errors,

\[ m_0^2 = e^2/\sum_1^1 1/w_1 \] (8)

whence

\[ \text{var}(c_1) = e^2/w_1 \sum_1^1 1/w_1 \] (9)

For a Gaussian error law the weights in (5) should be chosen inversely proportional to the variances. Equations (7) to (9) then become

\[ c_i = -\text{var}(d_1) e/\sum_1^1 (\text{var}(d_1)) \] (10)

\[ m_0^2 = Q = e^2/\sum_1 \text{var}(d_1) \] (11)

\[ \text{var}(c_1) = e^2 \text{var}(d_1)/\sum_1 \text{var}(d_1) \] (12)

For intercomparisons of equal precision unit weights are
assigned, the correction are equal, and their standard error is $e/\sqrt{3}$. The variance of the adjusted difference is then $(e^2/3 + \text{var}(d_1))$. A loop closure program has been written and shall now be outlined.

Subroutine SCLOSE( N, AB, DN, CLOOP, NAME)

**Purpose:** To perform the standard loop closure and related statistical calculations for three intercomparisons forming a closed loop containing samples A-B, B-C, C-A, and to prepare a final report sheet.

**Use:** A call for SCLOSE is best inserted in the MAIN LEAD REDUCTI-program (MLR) as the third last call, e.g.

```fortran
WRITE(6,4800) TIME
CALL SCLOSE(N,AB,DN,CLOOP,NAME)
GO TO 1
END
```

At call time the arguments contain the following information:

- **N** Number of pairs in a single or combined run;
- **AB** Abundances normalized in various ways;
- **DN** Standard deviations of the peaks of a pair in a run; or a combined run;
- **CLOOP** A logical variable. It must be read into MLR. If CLOOP is true, a loop closure calculation will be executed;
- **Name** Identification of run, same as in column 71 - 80 of each data card.

**Method:** Each call stores relevant information for one run. In the sixth call, CLOOP = .TRUE. initiates the calculation. The standard errors of the peaks are used as standard deviation of the abundances for weighting purposes. The standard error of the differences between runs are obtained from standard formulae for error propagation. The loop closure error is found and spread over the three intercomparisons
proportionally to their variances. The standard error of the adjusted difference is then calculated using equation (12) and the standard error of the differences.
APPENDIX II
THE PRESENT AUTOMATED REDUCTION PROCEDURE

At the time of writing this thesis a set of compatible programs for the automatic reduction of the trimethyllead spectrum had been set up. The programs are written in the Fortran IV language for the IBM-7040 computer. It is recognized that in some phases of the calculations savings in computer time can be obtained by making more efficient use of the machine features, but a major revision is not thought to be useful until the pending installation of a high speed paper tape reader in the Computing Center of this university has been completed. At present the data must be transcribed from paper tape to cards. To aid in the understanding of the present reduction system, and to facilitate the reprogramming which will become necessary, a short summary of the essentials of the reduction programs and the necessary flow chart, will be given in the following pages.

DW1 - An Independent Main Program.

**Purpose:** To read from cards raw mass spectrometer data; to check for, and create continuity of the data (cf. section 2.4.2); to check for and label switching transients according to a given relation (section 2.4.3); to search for a pair separator in the data, and to write the data in binary mode on magnetic tape.

**Use:** Specify number of files to be skipped before writing magnetic tape on first data card under Format (I3). Title cards may be present. They are specified by a 0-2-8 punch in
column 1, and can have an identification in columns 71-80. All other columns may carry any text. Only the text of the first 2 cards will be preserved on tape. A pair separator card must be inserted manually between scan pairs. This card has the letters PARSEP in columns 75-80. Behind the last pair an END-card takes the place of the PARSEP-card (columns 78-80). If another run (with a new set of title cards, if desired) follows the first, a NEWJOB-card is used instead of the END-card.

**Execution time:** about 11 sec per scan pair.

**ILOB2 - A Mainline Control Program**

**Purpose:** To control input to, and combine CALL's for reduction routines.

**Use:** Supply one card with the following information:

- **NSKP:** Filemarks to be skipped on magnetic tape.
- **NFLUSE:** Number of files to be used. (One file contains one complete analysis.)
- **PUNCH:** Logical variable: if "yes", data cards will be punched for input to MLR.
- **SR:** Sampling rate (per second).
- **PTSPMS:** Average number of data points per mass distance.
- **FROSIC:** Logical variable: if "yes" the height of peak 249 will be measured from a straight line between the minima adjacent to that peak.

The format for above information is (2I5,L5,2F5.2,L5).

Further, supply one card for each run to be reduced, containing an identification as used for MLR-data. If a COMBINE-card is to be produced, punch a "T" anywhere in columns 11-15 in the same card. (FORMAT(2A5,L5)).
Subroutines to be supplied:

RED: Reduction program 1
NTL2: Reduction program 2

Subroutine RED(SP,ISH,CHK,NDATA OPTION)

Purpose: Given a pre-processed (DW1) set of data, SP, and corresponding shunt letters, ISH, and check locations: to search for bases; to adjust bases with a least squares fit at the ends of each scan; to subtract bases from all readings and multiply by shunt factors; to interpolate switching transients and parity errors (in paper tape) linearly between adjacent readings.

Option: Set equal to +1.

Execution time: approx. 2.5 sec per pair.

Subprograms to be supplied: POLYP(NDATA,X,Y,ORDER, COEFFICIENTS), a least squares fitting program.

Subroutine NTL2(SP,ISH,NDATA,IDEM,PRSP)

Purpose: Given a scan pair (SP, SHUNTLETTERS, and a controlword (PRSP)): to reduce to peak heights; to calculate pressure factors and collect their statistics; to produce a complete set of data cards for input to MLR, if desired. (PUNCH = .TRUE.).

Execution time: approx. 21 sec per scan pair.

Subroutines to be supplied:

NULL (array resetting)
BUCH3 (scan selection)
PEKPS3 (peak positioning)
GERING (detection of minima)
HYPERB (hyperbolic interpolation)
FILTER (numerical filter)
MINTAL (optional, uses least squares for pressure corrections)
The following diagrams illustrate the data flow in the reduction programs. The symbols used are IBM standard.
Legend:

← Present data flow
←→ Suggested flow
←# Interruption of automatic flow

Figure A-1 Diagram of present automatic reduction system.
Figure A-2 Diagram of reduction control program ILOB2

1. **ENTRY ILOB2**

2. **READ:** NSK PFL NLUSE PUNCH OR PTSP MS FROSID

3. **FIND DATA ON TAPE**

4. **YES**
   - **CONTROL = NEWJOB**
   - **STOP**

5. **NO**
   - **FILE MARK COUNTER = NLUSE**

6. **READ:** IDENTIFY, COMBINE

7. **READ ONE SCAN PAIR FROM TAPE**

8. **YES**
   - **CONTROL = NEWJOB; INCREASE FILE MARK COUNTER**
   - **SENSE FILE MARK?**
   - **NO**
   - **BACKSPACE TAPE**

9. **NO**
   - **SENS•ED FILE MARK?**
   - **YES**
   - **CONTROL = PARSEP**

10. **CALL NTLB**

11. **CALL RED**
INDEX OF NOTATIONS

\( a_1 \) peak amplitudes,

\( a(t) \) set of impulse functions of values \( a_1 \),

\( A \) Fourier transform of set of impulse functions,

\( b_1 \) background signal under the \( i \)-th peak (Section 3.4.2); constant, related to signal representing zero ion current,

\( B \) output signal for zero ion current,

\( C \) crosscorrelation,

\( D_0 \) boxcar function (Blackman and Tukey, 1958, p.68),

\( D_i \) height of peak tail \( i \) mass units downmass (esp. \( D_3 \)),

\( E \) general constant,

\( f \) frequency, usually as an argument; an artificial record,

\( \mathcal{F}, \mathcal{F}^{-1} \) Fourier transform and its inverse,

\( F \) general constant,

\( g \) ion beam shape,

\( G \) Fourier transform of a beam shape, \( g \),

\( i \) \( \sqrt{-1} \); ion current,

\( K \) general constant,

\( \ln \) natural logarithm,

\( n \) sequence number of data point, proportional to time,

\( N \) number of data in the record,

\( p \) peak shape,

\( P \) pressure in analyser tube,

\( P \) Fourier transform of peak shape; pole of the hyperbolic peak tail representation,

\( Q \) sum of squared errors, \( \sum \epsilon^2 \),
ratio of effective ion beam width, \( s \), to collector slit width,

attenuation factor for different sensitivity measuring ranges,

effective halfwidth of a Gaussian ion beam,

time; often more generally the experimental variable related to time,

collector slit width,

ion beam width,

Fourier transform of collector slit,

tail height at one mass distance, usually with subscript; general time-like variable,

the recorded signal; height of peak tail at two mass distances, usually with subscript \( d \) or \( u \), for downmass and upmass,

Fourier transform of recorded signal,

numerically filtered record,

Fourier transform of numerically filtered record; zero of peak tail, extension of peak tail,

interval,

2\( \pi \) frequency,

residual, difference between actual and artificial records,

sign of convolution; also sign of correlation, e.g. \( f(x) \ast g(-x) = \text{crosscorrelation of } f(x) \text{ and } g(x) \).