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THE QUANTITATIVE MASS SPECTROMETRIC DETERMINATION OF TRACE IMPURITIES IN URANIUM HEXAFLUORIDE USING RELATIVE RESPONSE FACTORS

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THE QUANTITATIVE MASS SPECTROMETRIC DETERMINATION OF TRACE IMPURITIES IN URANIUM HEXAFLUORIDE USING RELATIVE RESPONSE FACTORS

by

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ABSTRACT

A method has been developed that uses uranium hexafluoride as the internal standard to quantitatively determine trace impurities in the uranium hexafluoride using relative response factors. A computer program was written to control the mass spectrometer and determine the concentrations of target impurities present. Overlapping spectra are deconvoluted using the Gauss-Seidel iterative method. The composition of the sample is determined by comparing the peak height ratios of the target impurities to the internal standard.

Measurement parameters are easily modified using the menu driven program. A flexible database allows the list of target impurities to be extended to accommodate any changes in analytical requirements. The method has been adapted for automatic on-line measurements.

The technique was evaluated by analysing a number of carefully prepared standards. Nine target impurities were studied which ranged in concentration from parts per million to percentages. An overall precision of fifteen percent was obtained.

SAMEVATTING

'n Metode is ontwikkel wat uraanheksafluoried as 'n interne standaard gebruik om spooronsuiwerhede kwantitatief met behulp van relatiewe responsfaktore in die uraanheksafluoried te bepaal. 'n Rekenaarprogram is geskryf om die massaspektrometer te beheer en die konsentrasies van teikenonsuiwerhede te bereken. Spektra wat oorvleuel word wiskundig met behulp van die Gauss-Seidel iterasiemetode geskei. Die samestelling van die monster word bereken deur die verhoudings van piekhoogtes van die teikenonsuiwerhede teenoor die interne standaard te vergelyk.

Ontledingsparameters word maklik met behulp van die spyskaartgedrewe program verander. 'n Buigsame databasis maak voorsiening vir 'n uitbreiding van die lys van teikenonsuiwerhede, as gevolg van veranderinge in analitiese behoeftes. Die metode is vir outomatiese inbaanontledings aangepas.

Die tegniek is deur die ontleding van 'n aantal noukeurig-bereide standaarde geëvalueer. Nege teikenonsuiwerhede wat in konsentrasie van dele per miljoen tot persentasies gewissel het, is ondersoek. 'n Algehele presisie van vyftien persent is verkry.

ABBREVIATIONS AND CONVENTIONS USED

AEC	Atomic Energy Corporation of SA Ltd.
BFB	Bromofluorobenzene.
DC	Direct current.
DIPE	Di-isopropyl ether.
EI	Electron impact. An ionisation technique where ionisation is caused by a stream of electrons striking the sample.
EPA	United States of America Environmental Protection Agency.
eV	Electron volts.
Freon-11	Freons are a general class of halogenated refrigerants. The general formula is Freon xyz, where: C = x + 1; H = y - 1; F = z and Cl = 2x - y - z + 5. Therefore, Freon-11 is $CFCl_3$.
IUPAC	International Union of Pure and Applied Chemistry.
m/e	The mass-to-charge ratio, measured in Daltons.
MHz	A measurement of frequency, 10^6 cycles per second.
PC	Personal or micro computer.
ppm	Parts per million, or micro moles per mole UF_6.
r	The correlation coefficient determined using linear regression analysis.
RF	Radio frequency.

RSD	The relative standard deviation expressed as a percentage, = 100 x standard deviation / mean.
RRF	Relative response factor.
RRF_{is}	The relative response factor of compound i in relation to compound s.
RRF_i	The relative response factor of compound i in relation to the internal standard, $^{235}UF^{2+}$, divided by the ^{235}U isotopic concentration. All five $^{235}UF_x^{2+}$ internal standards are used during an analysis, however, for reasons of clarity the RRFs were only determined relative to $^{235}UF^{2+}$.
SEM	Secondary electron multiplier.
STP	Standard temperature and pressure
s	Standard deviation.
s_{yx}	The standard deviation or error of the slope of a line determined using linear regression analysis.
UF_6	Uranium hexafluoride.
UF_x^{2+}	A general description of the five internal standard peaks used where x is an integer from 0 to 4.
$\bar{x}$	The average, or mean of a group of observations.

CHAPTER 1
INTRODUCTION

The nuclear industry demands high quality control standards in all facets of production, including the accurate monitoring of trace impurities in the natural uranium hexafluoride feed material of enrichment plants. Impurities in some cases have detrimental effects on the enrichment process and strict quality assurance measures are required. Mass spectrometry is an ideal technique for this application, as it requires no prior separation or sample preparation and has high sensitivities for a range of compounds.

Mass spectrometry does not easily lend itself towards automation as there are a number of factors which if not carefully controlled can adversely affect the accuracy of the results. While this supervision is obtainable under laboratory conditions, it is especially difficult when the instrument is used unattended for process control.

The use of electron bombardment mass spectrometry for quantitative analysis depends on the unique mass pattern generated from individual compounds. Except for certain types of geometric isomers, for example, cis-trans isomers, the relative intensities of the fragment ions constitute a unique "fingerprint", which can be used for identification of an unknown compound by comparison with mass patterns of known standard materials. For quantitative purposes, each component in a mixture is assumed to contribute to the mass pattern according to its partial pressure. Thus the measured mass spectrum is treated as a linear superposition of mass patterns according to the partial pressures of the mixture.

Quantitative analysis presupposes qualitative analysis. Therefore, unless

the components of the mixture are known prior to the analysis, the components must first be identified from the mass spectrum[1]. Consequently, the interpretation of mass spectra is essentially the solution of systems of linear equations, which in principle can be performed by a computer, provided that the individual fragment spectra and calibration response factors are known. A number of factors could significantly influence the accuracy of the method. The fragmentation pattern is dependent on external factors [2] such as the ionisation energy and source temperature, and therefore literature data can only be regarded as an approximation for quantification purposes. As some elements are not mono-isotopic, a chemically pure compound has a mass spectrum that includes fragments from the various isotopes. The fragmentation pattern from isotopic fragments are largely independent of external factors as the fragments are chemically similar and have similar masses. Wherever possible they should be utilised for calculations. Fractionation due to gas-flow effects of lighter isotopes could influence the results[3] slightly, although this is minimal in comparison to the source effects mentioned above.

The quantification process indicates which compounds are present and the extent to which each compound contributes to the total mass spectrum. Peak intensity data must be translated into concentration by a calibration process. The standard method of quantifying an unknown spectrum involves the use of calibration curves. To remain accurate, the calibration has to be performed regularly as fluctuations in the ion signals occur, due to changes in the electrostatic focusing conditions and detector sensitivity with time. This is time consuming and entails the mixing of standards and measuring these on a regular basis. Work practices at the Atomic Energy Corporation of South Africa Limited (AEC) laboratories, prior to implementation of the relative response method, involved the preparation and measurement of five standards

each week, in addition to a control sample that was analysed with every sample batch using a two parts per million (ppm) mixture of both chlorine and Freon-11 in UF_6.

An alternative method of quantifying an unknown compound is the use of an internal standard. In this method, in general terms, a fixed amount of a known compound is added to the unknown sample and the intensity of the instrument signal is compared with the intensities of compounds in the unknown sample. An example of this method is the addition of fluorinated hydrocarbons which do not occur naturally, to a sample of organic substances[4]. The signal from the sample is compared with the signal from the fluorinated compound and the concentration can then be calculated, provided that the relative response factors of the internal standard and the target impurity have been predetermined.

Spark source mass spectroscopy is an example where quantification is done with an internal standard. A radio frequency electric discharge is used to ionise the molecules in the ion source. The ion signal in this case is highly dependent on instrument parameters such as the electrode gap, and it is therefore better to use an internal standard[5]. Internal standardisation is most effective when the analytes and internal standards are closely matched in terms of mass and ionisation potential[6], and the major matrix element is the preferred internal standard[7, 8].

The UF_6 samples submitted for impurity analysis at the AEC normally contain only trace impurities, i.e. in the ppm range. It is required that the samples be analysed with an accuracy equal to or better than that of the standards used for calibration (relative standard error of twenty percent). Furthermore, it is preferable that the samples are analysed

within two hours.

To achieve these goals, a study of the fundamentals of quadrupole mass spectrometry was undertaken. The following principles are discussed in chapter 2:

- During ionisation of the sample, a number of fragments are produced. This yields a collection of signal intensities at different mass-to-charge (m/e) ratios. These results are referred to as the mass spectrum. The signal intensities are measured according to ion counts and expressed as either a current or transferred to a voltage. The m/e ratio is measured in Daltons;
- Ion separation where the ions are separated according to the m/e ratio;
- There is normally a large amount of peak overlap in the mass spectrum as a result of the number of impurities present in the sample. Methods to resolve this overlap are described with attention given to the Gauss-Seidel iteration method as the preferred deconvolution routine;
- Calibration is usually performed either with internal or external standards. Internal standards have major advantages and are used by this analytical method. The theory of relative response factors is described;

The instrumentation and experimental procedures are described in chapter 3 which consists of three major sections:

- All major components of the apparatus are described. Mention is made of the initial state of the instrument, where the mass spectrum was produced on a recorder and concentrations were determined from the spectrum using external calibration, to the present computer controlled system;

- A description of the SCAN program:
  - The Gauss-Seidel deconvolution procedure is described, as applied by the SCAN procedure with boundary conditions imposed between a zero concentration and the highest possible concentration in the sample. This is determined by the two most significant masses per target compound investigated and is used as the initial estimate for the iteration process;
  - The major matrix element in the sample, UF_6, is used as the internal standard. The $^{235}UF_x^{2+}$ fragments are used for calibration as their masses and intensities are similar to those of the impurities;
  - Section 3.2.3 describes the main logic and functions of the SCAN program;
  - The SCAN program is designed to be operated with the minimum of operator intervention. Consequently there are only two menus. The main menu is used regularly whilst the second menu is used mainly to modify datafiles. Both menus are described in section 3.2.4;

- The experimental procedure describes:
  - The mass spectrometer operating conditions;
  - Initialisation of the data files used;
  - Preparation of samples and standards;
  - The analysis procedure;

Factors that could influence the accuracy of the result were investigated and are discussed in chapter 4. Conclusions are presented in chapter 5 together with refinements to the method that were gained from the operational period of five years. An analysis result form is shown in appendix A. The SCAN program is listed in appendix B.

CHAPTER 2

THEORETICAL PRINCIPLES

2.1 Ionisation and fragmentation

In an electron impact (EI) ion source, low-voltage (thermal) electrons are produced by heating a small tungsten or rhenium filament. These electrons are accelerated towards a cathode at about 50 to 100 eV. The electrons collide with a stream of gaseous molecules and ionisation occurs as the energy is transferred from the electrons to the molecules, causing an electron loss and/or fragmentation of the molecule. The ionisation/fragmentation process begins at a minimum electron energy (ionisation or appearance potential), and the number of ions formed grows rapidly with increasing energy, reaches a maximum and then slowly decreases [9].

When complex molecules are ionised, the number of possible ionic species grows rapidly with increasing complexity. Apart from the molecular ions with single or multiple charges, fragmentation and rearrangement of the molecule occurs. In Figure 2.1, the mass spectrum of UF_6, peaks from three distinct processes can be distinguished:

- multiply charged, e.g. UF_2^+, UF_2^{2+} and UF_2^{3+};
- fragmentation, e.g. U^+, UF^+, UF_2^+ , UF_3^+ and UF_4^+;
- and isotopic composition, e.g. $^{238}UF_5^+$ and $^{235}UF_5^+$.

The occurrence and relative abundance of the various kinds of ions is characteristic for each kind of molecule and these data can be found in literature compilations. The data are only an approximation, as the fragmentation pattern is dependent on external factors, such as the ionisation energy and must be compared at a specific ion energy.

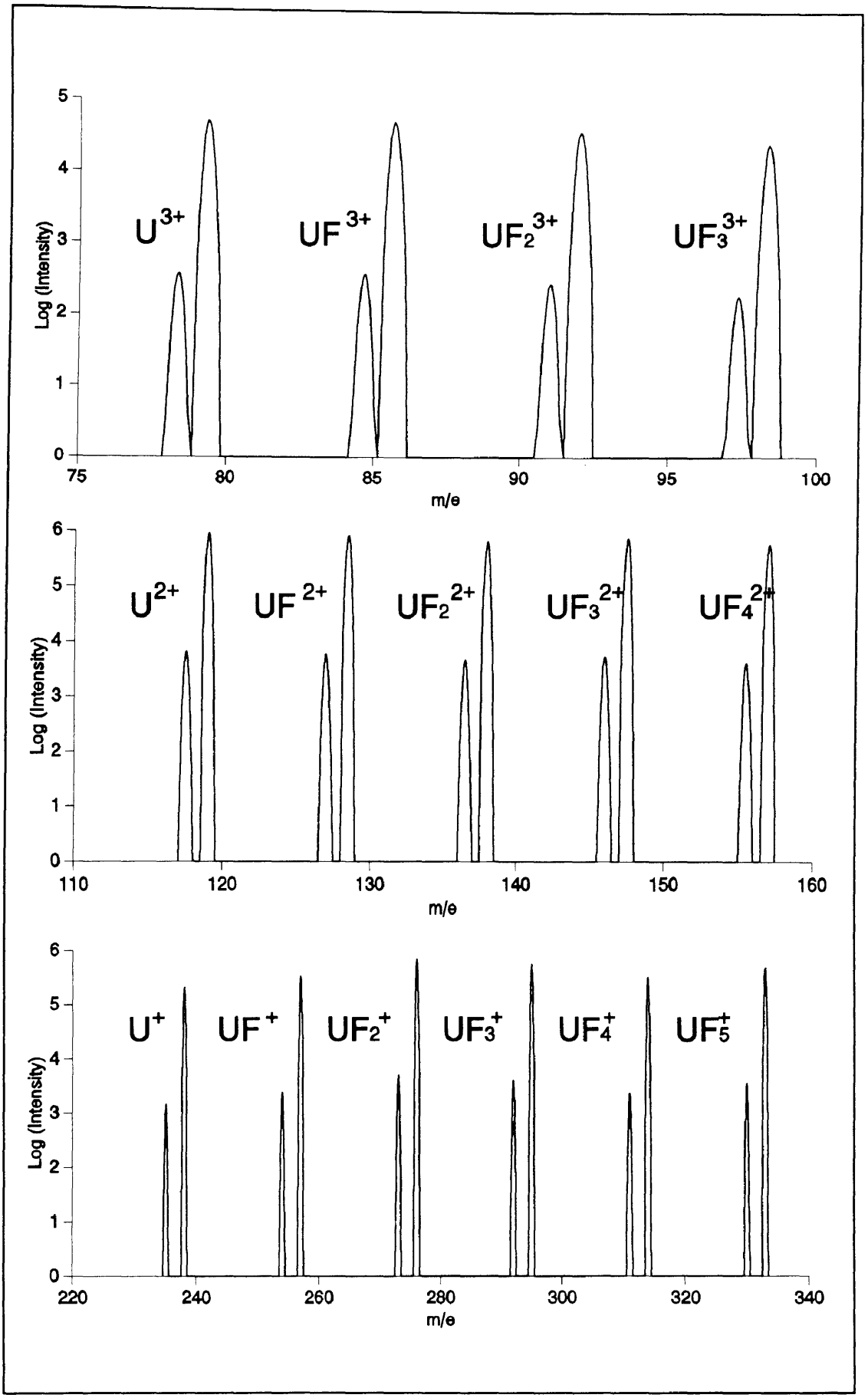


Figure 2.1 Mass spectrum of UF_6

2.2 Ion separation

After the sample has been ionised, the fragments have to be separated. This is achieved through the use of magnetic and/or electric fields. The two most common instruments used are the sector and quadrupole instruments. The sector instruments rely on powerful magnets to curve the flight path of the fragments to the detector. In comparison, the quadrupole instruments apply electrostatic fields to achieve stable and unstable ion trajectories.

Quadrupole mass analysers represent more than 80% of the mass spectrometer market, since they predominate in the high volume, low cost applications[10]. In addition, they have adequately high sensitivities, are light weight, use low potentials in the ion source and are capable of very fast scan speeds, by virtue of the fact that the masses are scanned by varying the applied direct current (DC) and radio frequency (RF) voltages, both of which can be changed quickly and accurately. This scan dependence on the DC and RF field accounts for the popularity of the quadrupoles and has the following advantages:

- Peak widths are constant over the mass range;
- Mass calibration is easy and extremely stable;
- Control of the mass is easy to adjust automatically;
- No magnetic field hysteresis;
- Selected ion monitoring is fast and accurate.

For low resolution analyses, the quadrupole yields similar results to that of a sector instrument, although the precision is worse[11]. The traditional magnetic sector mass spectrometers still reign supreme in high resolution applications, which require the direct determination of the elemental composition of organic compounds[10].

The ability of the quadrupole mass analyser to resolve ions, depends critically on the uniformity of the electrostatic field within the analyser[12]. Ideally, the four rods should have hyperbolic surfaces to establish the quadrupole field without distortions. Technically this is difficult to achieve and most of the commercially available instruments have compromised between the ideal and cost by employing very accurately machined rods of circular cross section. Field distortion may give rise to peak-splitting where the recorded trace appears as a series of closely spaced multiplets.

The quadrupole analyser essentially consists of a source in which the ions are generated, the rod system which separates the ions according to the mass-to-charge ratio, and a detection system that measures the ion currents. The quadrupole mass analyser was originally proposed by W Paul[13, 14], and operates on the same general focusing principles as those for a high-energy accelerator using a strong focusing alternating gradient field. These principles are:

- The restoring force on an ion increases in proportion to it's displacement from the axis of the field;
- there is a net focusing effect on the ion beam by alternately increasing and decreasing the forces on the beam.

In the quadrupole mass analyser, the alternation is applied electronically and the field varies with time, by an applied RF voltage to the quadrupole electrode rods. Figures 2.2 and 2.3 show the basic structure of the analyser.

Focusing occurs simultaneously in two dimensions at right angles to the axis of the field and out of phase with each other. The voltage between the electrodes is composed of a high frequency alternating component,

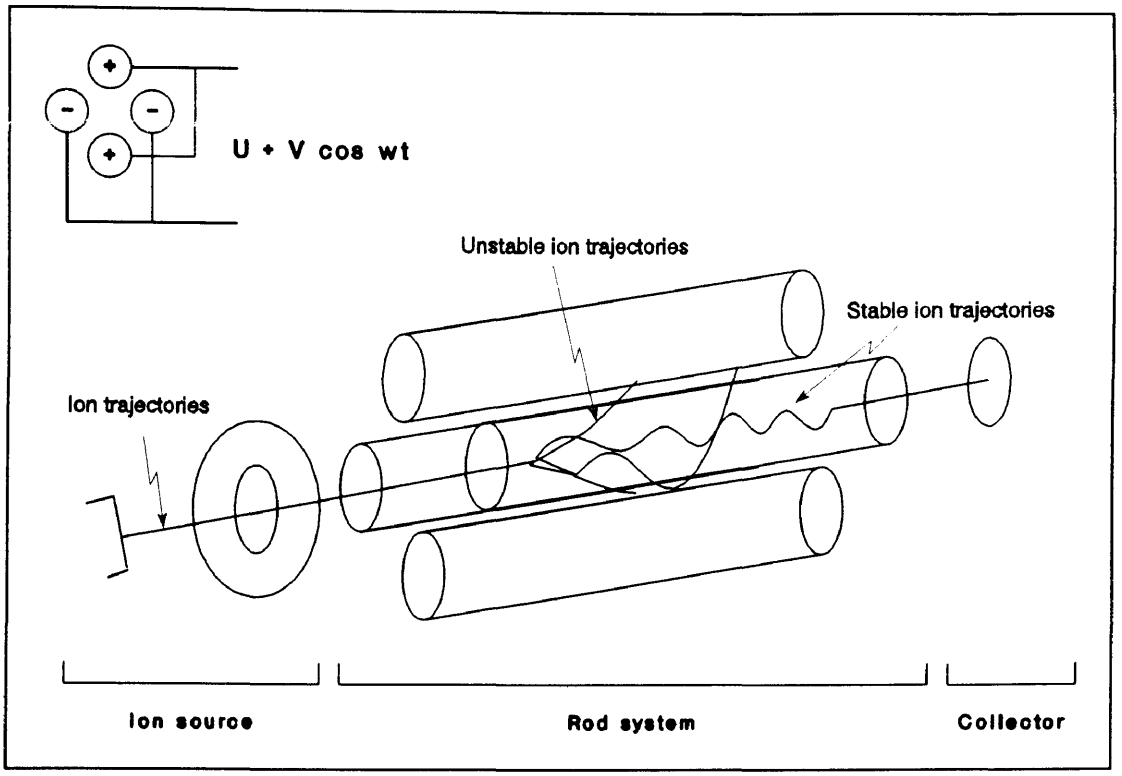


Figure 2.2 Basic structure of a quadrupole analyzer

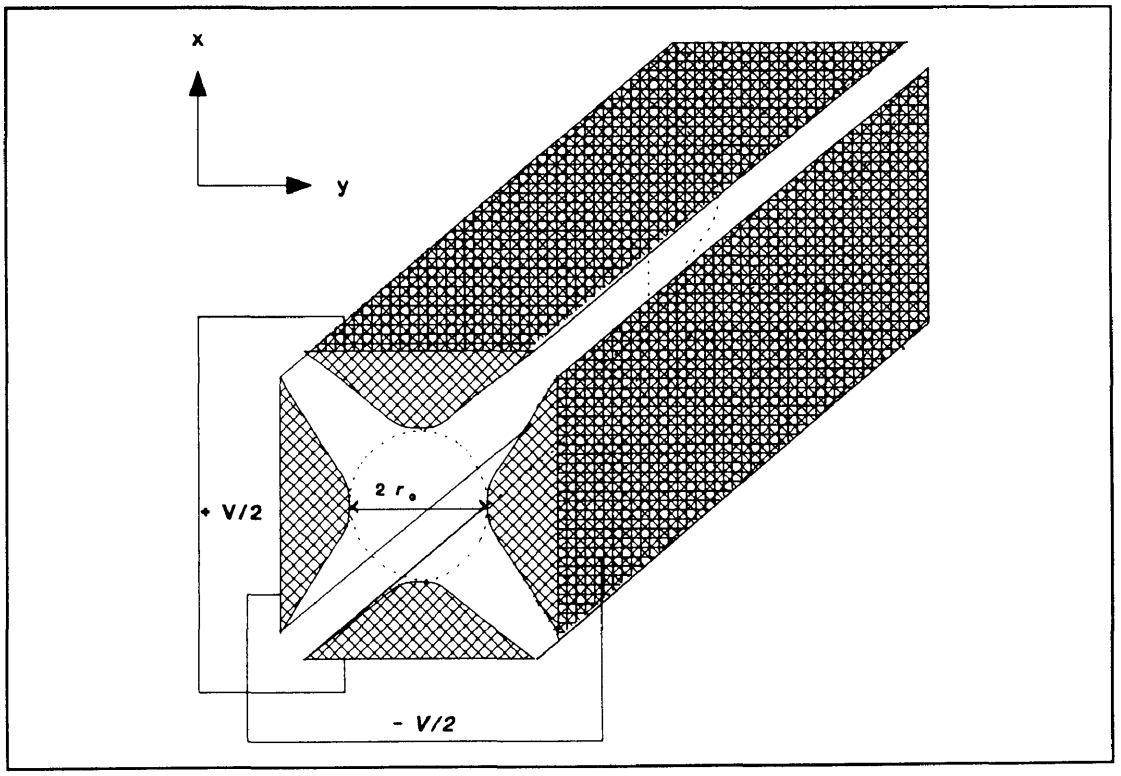


Figure 2.3 Field generating potentials

V cos ωt, and a superimposed direct voltage, U.

If ions in the direction of the axis of the field are injected into the mass filter, the influence of the high frequency electric field causes them to oscillate at right angles to this axis[10].

The equations of motion of these ions are defined by Mathieu differential equations, the solutions of which are known and are classified into two groups. If the amplitude of oscillation remains constant, these are called stable solutions. However, if the amplitude of oscillations increases with time, these are referred to as unstable solutions. Consequently, some ions would pass through the mass analyser while the increasing amplitude of motion of the other ions would cause them to collide with the rods and be neutralised and pumped away by the vacuum system. Reference 15 provides a comprehensive description of the theory of ion separation in a quadrupole field. For clarity, this description is given below without significant amendment. As the theory of mass separation using quadrupole fields is extremely complex, only a general description is given.

The stability diagrams (Figure 2.4 and 2.5) show how the transmission of an ion in the quadrupole field varies with the operational parameters.

$$q = 2\ eV/mr_0^2\omega^2 \quad \text{and} \quad a = 4\ eU/mr_0^2\omega^2$$

where:

- m is the mass number of the ions in Daltons;
- V is the amplitude of the RF voltage component;
- U is the amplitude of the DC voltage component;
- ω is the applied frequency in MHz;
- r_0 is the field radius in cm;
- e is the charge of the ion.

When the parameters V, U, ω and r_0 are given, only ions in a definite mass interval are able to pass through the separating field. The amplitude of oscillation of these ions remains finite and smaller than r_0. All other ions strike the rods and are pumped out by the vacuum system. U is kept in a fixed proportion to V (that is $U = kV$ with k determining the resolution or mass interval to be transmitted). When the ratio of U/V is kept just below 0.1678 the relationship that gives stable trajectories for ions can be simplified to[9]:

$$V = 14.4\ m\ \nu^2\ r_0^2 \qquad \text{(frequency } \nu = \omega/2\pi\text{)}$$

The mass to be transmitted can be scanned by varying the frequency ($m \approx 1/\omega^2$) or by varying the voltage ($m \approx V$).

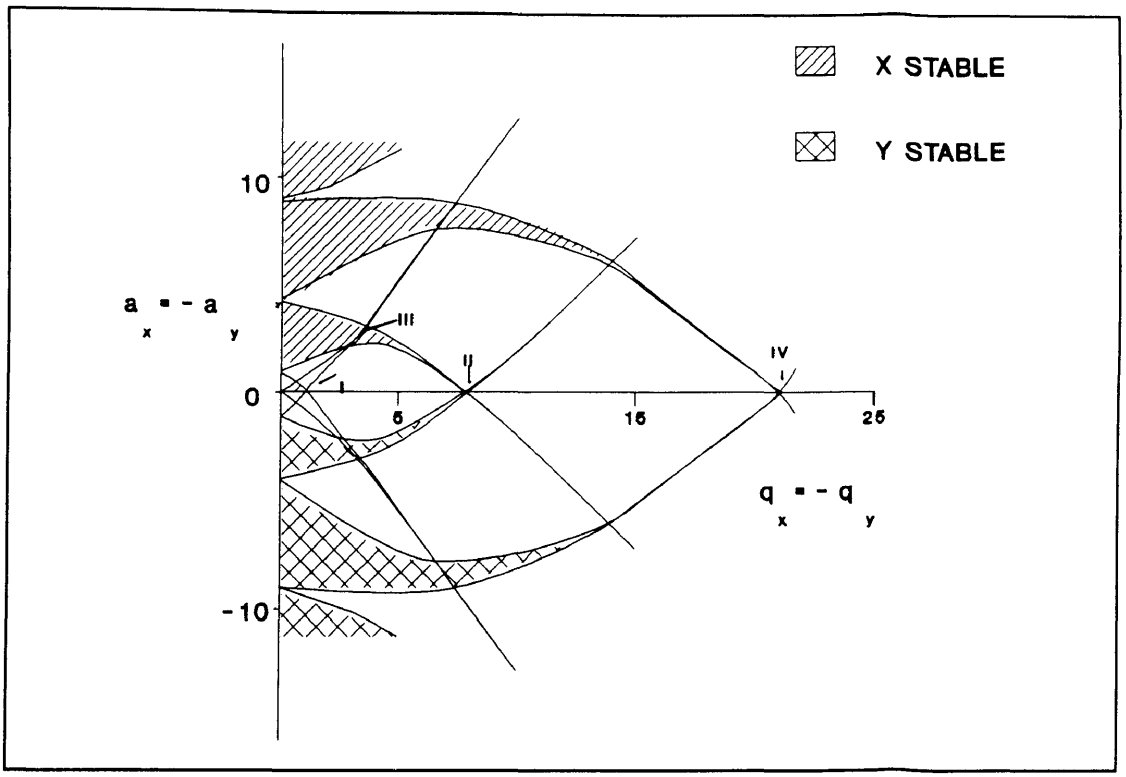


Figure 2.3 The stability diagram for the two-dimensional case where the x and y directions differ by a factor of -1. The first stability region is enlarged below.

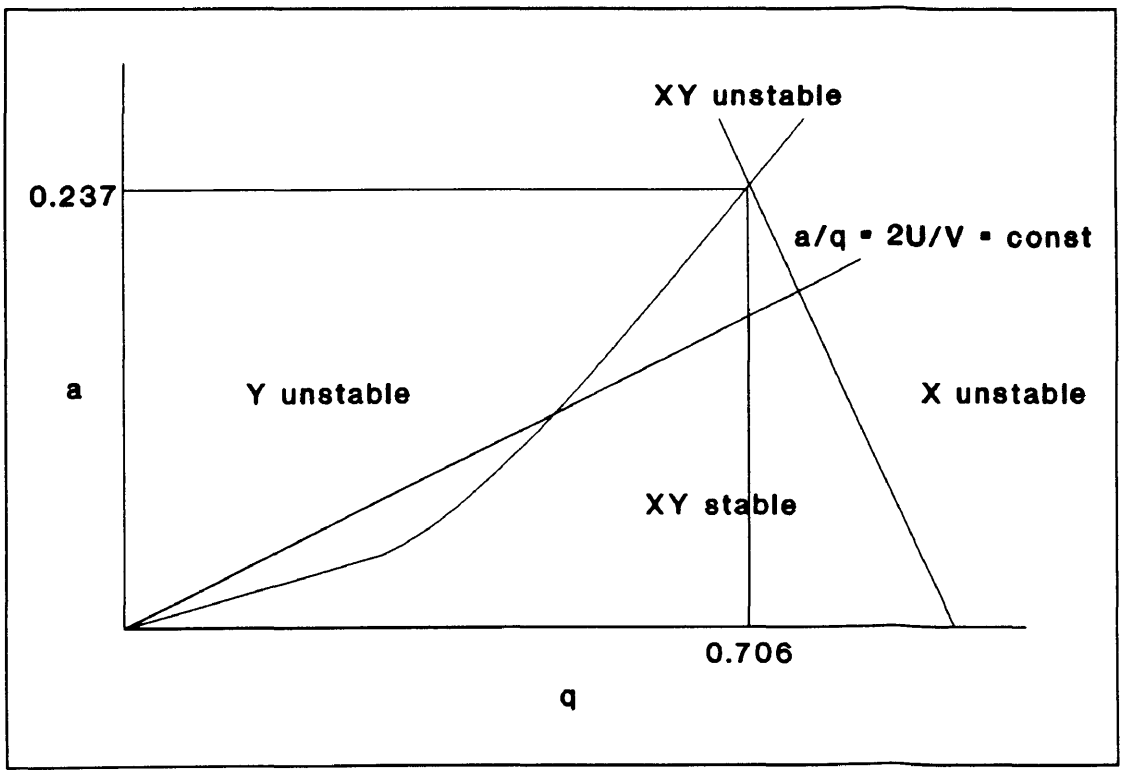


Figure 2.4 Enlargement of the first stability region

2.3 Peak separation

One might expect that the mass spectra would provide quantitative details of the sample composition through partial pressures relating to concentrations. Unfortunately, due to peak overlap, only intensities associated with definite mass numbers are obtained.

The degree of overlapping is dependent on the resolution of the instrument, where the resolution is the ability to distinguish between two closely spaced ions, and is defined as: $R = m/\Delta m$. A standard definition for Δm has not been adopted and can be measured by reference to one or two peaks. For example, the 10% valley definition applies where two peaks of equal size are considered to be resolved if they are separated by a valley of 10% of the peak height. Each peak makes a 5% contribution to the formation of the valley (Figure 2.6). From the figure it can be seen that Δm can be measured from the separation of two peaks using the 10% valley definition, or by measuring the width of a single peak at 5% height[16]. Quadrupole instruments are normally operated at a constant Δm, (measured at 50% peak height), over the whole mass range. This means that the resolution, as defined above, increases with mass in the quadrupole. In the case of the magnetic sector instruments the resolution is unaffected by the mass.

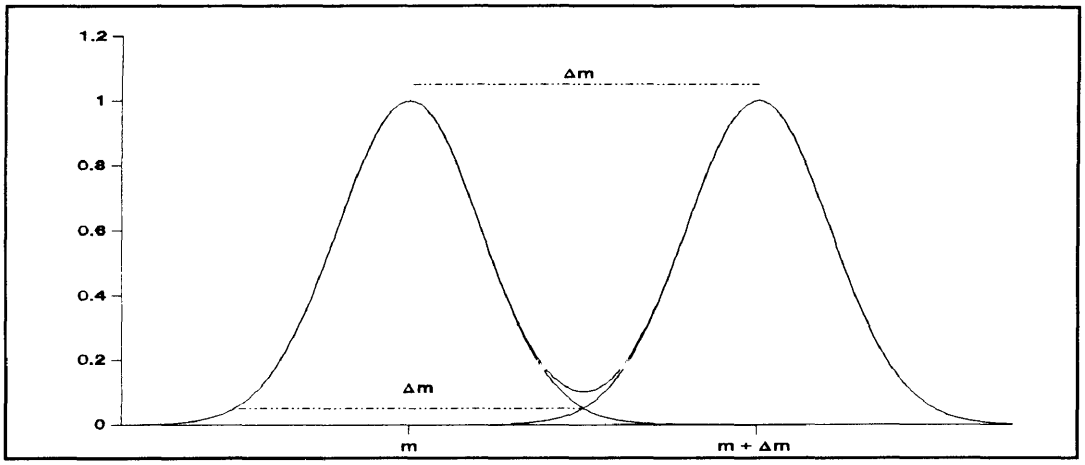


Figure 2.6 Defining resolution according to Δm

With a high resolution instrument, the resolution might be sufficient to separate two components such as N_2 and CO at 28.00615 and 27.99491 Daltons, respectively, which requires a resolution of 2490[16]. In comparison, the resolution of the quadrupole instrument is at best 50 for these low masses. In general, a quadrupole can only separate masses of different integer m/e values. Due to the generally low resolution, there is far greater overlap of peaks in a quadrupole instrument, and the derivation of concentrations from such data requires careful calibration and extensive computing in complicated cases.

Occasionally, the different gases in the sample may be identified from their characteristic masses without having to make corrections for mutual interferences. However, if many different gases are present, the measured peak intensities are linear combinations of their individual contributions[17]. The spectra become more complex for higher mass compounds through greater overlapping of peaks. Table 2.1 shows the fragmentation distribution[18] of some common low molecular mass gases, indicating the complexity of the spectra. The mass number is the mass-to-charge ratio of the fragment.

The availability of high speed computers with large, fast memory access capabilities, has made it possible to obtain accurate numerical solutions to mathematical problems which, although the algorithms are well known, could not until recently be used in practice because the number of calculations would have been prohibitive. A problem for which this is particularly true, is that of solving a large system of linear algebraic equations, where the matrix of the system is very "sparse", that is where most of the elements in the matrix are zero. Solutions to these systems are better obtained by an iterative approach such as the Gauss elimination method, rather than with a direct matrix reduction method[19].

Table 2.1 Relative ion currents (peak heights) of ions found in the mass spectra of some lighter gases.
The most intense peak is given the value of 100

Mass number	H_2	He	CH_4	H_2O	Ne	N_2	CO	O_2	Ar	CO_2
1	3		16.5							
2	100			2.4						
3		100								
12			3				6.3			9.7
13			7.8							
14			16			14	0.8			
15			85							
16			100	1.8			2.8	1.8		16
17			1.2	26						
18				100						
20					100				22.6	
22					10.2					2.1
28						100	100			13
29						0.7	1.2			
32								100		
34								0.4		
36									0.34	
38									0.06	
40									100	
44										100
45										1.2

The Gauss elimination method suffers from two major disadvantages: round-off errors, although minimised by pivoting, can be large, and Gaussian elimination involves movement of data in the matrix.
For example, several rows may need to be interchanged. This is time consuming and also creates round-off errors. In comparison, iterative methods require fewer arithmetic operations and round-off errors are almost entirely eliminated, being only committed in the final iteration.

Iterative methods involve the solution of an initial approximation of U(0) to the general matrix equation of: AU = B, where:

- A is a given real NxN matrix;
- B is a given real column of order N;
- U is the unknown column vector to be determined.

The sequence U(1), U(2) ... is determined in accordance with an algorithm, which if chosen correctly, will converge to the exact solution of U. The use of such an algorithm has the advantage that the matrix A is not altered during computation. Hence, though the computation may be long, the problem of accumulation of rounding-off errors is less serious than for other methods, such as most direct methods where the matrix is changed during the computation process. In the Gauss-Seidel iteration method, each element in the solution matrix is updated as soon as it is calculated[19]. This differs from the normal iterative method where the solution matrix is only altered after all elements in the matrix have been determined. Consequently, in the Gauss-Seidel iteration method, fewer steps are needed to converge to the exact result.

2.4 Relative response factors

The intensity of a fragment ion in the mass spectrum is dependent on the probability of the parent molecule being ionised in the EI ion source, and the probability of forming the fragment under consideration. This is dependent on[20]:

- The size of the molecule, the ionisation cross-section (Q), which is the sum of the atomic cross-sections of each atom in the molecule;
- The number of moles of the species in the ion source (N);
- The ionisation path length of the electrons, which is related to the design of the instrument (k);
- The degree of fragmentation, which is related to the energy of the electrons, and the bond strengths of the molecule. This is the amount of a particular ion formed, expressed as a fraction, DF, of all molecules initially ionised.

After the molecule has been ionised, it must be focused and extracted out of the ion source, through the quadrupole rods and to the detector. Different masses have different probabilities of transmission to the detector, and the resulting mass dependent discrimination will change the observed relative ion intensity[8].

The total ion current for a given mass range (absolute molar response) can be expressed as $I_i = k \cdot Q \cdot DF \cdot N$. If no mass dependent discrimination occurs, the instrument parameter, k, will be constant for all molecules. However, as the instrument becomes contaminated, this parameter will decrease, resulting in a drop in signal strength. If I_i is measured relative to a standard, this instrument related parameter can be eliminated. This relative molar response (RMR) is then only dependent on parameters related directly to the molecule and will therefore remain constant.

Unfortunately, if the effect of mass discrimination is taken into account (which can vary with the state of contamination of the instrument), the RMR can change with time.

$$RMR_{is} = \frac{I_i}{I_s} = \frac{k\ Q_i\ DF_i\ N_i}{k\ Q_s\ DF_s\ N_s}$$

$$= \frac{Q_i\ DF_i\ N_i}{Q_s\ DF_s\ N_s}$$

$$as \quad \frac{N_i}{N_s} = \frac{[i]}{[s]}$$

$$\therefore \frac{I_i}{I_s} = \frac{Q_i\ DF_i\ [i]}{Q_s\ DF_s\ [s]}$$

The relative response factor (RRF) can be defined as [10] :

$$RRF_{is} = \frac{\frac{I_i}{[i]}}{\frac{I_s}{[s]}}$$

$$= \frac{I_i\ [s]}{I_s\ [i]} \qquad (1)$$

$$= \frac{Q_i\ DF_i}{Q_s\ DF_s}$$

where:

- RRF_{is} is the response of compound i relative to s, the standard;
- I_i and I_s are the ion signals of i and s respectively, after blank subtraction;
- [i] and [s] are the concentrations of i and s in the sample in moles per litre.

When UF_6 is used as the internal standard, equation (1) becomes:

$$RRF_{i\ UF_6} = \frac{I_i\ [UF_6]}{[i]\ I_{UF_6}} \qquad (2)$$

This parameter can be determined relative to a number of selected peaks in the UF_6 mass spectrum, by measuring a sample of known composition. If $RRF_{i\ UF6}$ is known, then the concentration ratio can be determined in a sample of unknown composition.

$$\frac{[i]}{[UF_6]} = \frac{I_i}{I_{UF_6}\ RRF_{i\ UF_6}} \qquad (3)$$

CHAPTER 3
INSTRUMENTATION AND EXPERIMENTAL PROCEDURE

3.1 Apparatus

The instrument was assembled in-house, using a commercial analyser and vacuum pumps. The inlet system, liquid nitrogen system and cold traps were designed and manufactured in-house. Prior to the implementation of this method, the analysis of Cl_2 and Freon-11 was done using a recorder. The first step in automating the process was the purchase of the "QUADSTAR" program from the manufacturers of the analyser.

The major disadvantage of this program was that only masses and intensities were obtained. A second program had to be written to read the QUADSTAR ASCII data file to determine the concentrations. This method was most efficient if the blank, standards and samples were collected on one data file and then subsequently analysed with the second program.

However, the method suffered from the following disadvantages:

- The time consuming and complex procedure required a reasonable knowledge of DOS;
- Over/under ranged samples were a problem;
- The program was limited to sixteen mass ranges;
- The QUADSTAR program "hung" regularly which lost all the data acquired.

Although the manufacturers introduced a new version of the QUADSTAR program, studies of the documentation indicated that the method would not be totally satisfactory for the requirements of the

AEC. A detailed investigation of the requirements, both present and future, was undertaken. Literature was consulted to address these requirements in the best manner possible. From those studies the present method was developed and the SCAN program was written to automate the analysis method. After a trial period during which the method was tested, it was decided to use the program to monitor the impurities in the UF_6 on-line . Apart from extra communication to the control room and the valve control unit, no major changes were made to the SCAN program. The SCAN program is discussed in detail in the next section.

The mass spectrometer system can be divided into four main sections (Figure 3.1). These are the vacuum system, inlet manifold, quadrupole analyser and electronic control systems. Vacuum is obtained on the inlet by a rotary pump evacuating through a series of two liquid nitrogen cold traps. Residual sample gas is first pumped away through this inlet vacuum system (HV). After most of the gas is pumped away ($<$ 0.1kPa), a second vacuum line is opened (HV1) which passes through a third liquid nitrogen trap to an ion pump of 8 ℓ/s capacity. The ultra high vacuum of 1×10^{-5} Pa in the analyser, is obtained by a small liquid nitrogen cold trap in the ion source housing, followed by an ion pump of 60 ℓ/s capacity.

Samples are connected to one of three inlet ports on the manifold. After the trapped air has been evacuated, the sample gas is expanded into the inlet manifold. From there the sample gas is introduced via a variable leak, into a tube that extends into the ion source. The variable leak controls the amount of gas which is fed into the ion source chamber, ensuring a stable signal during measurement and the buffering of minor sample pressure fluctuations. The tube causes considerable collimation of the gas flow at its exit to guide the corrosive beam of gas through

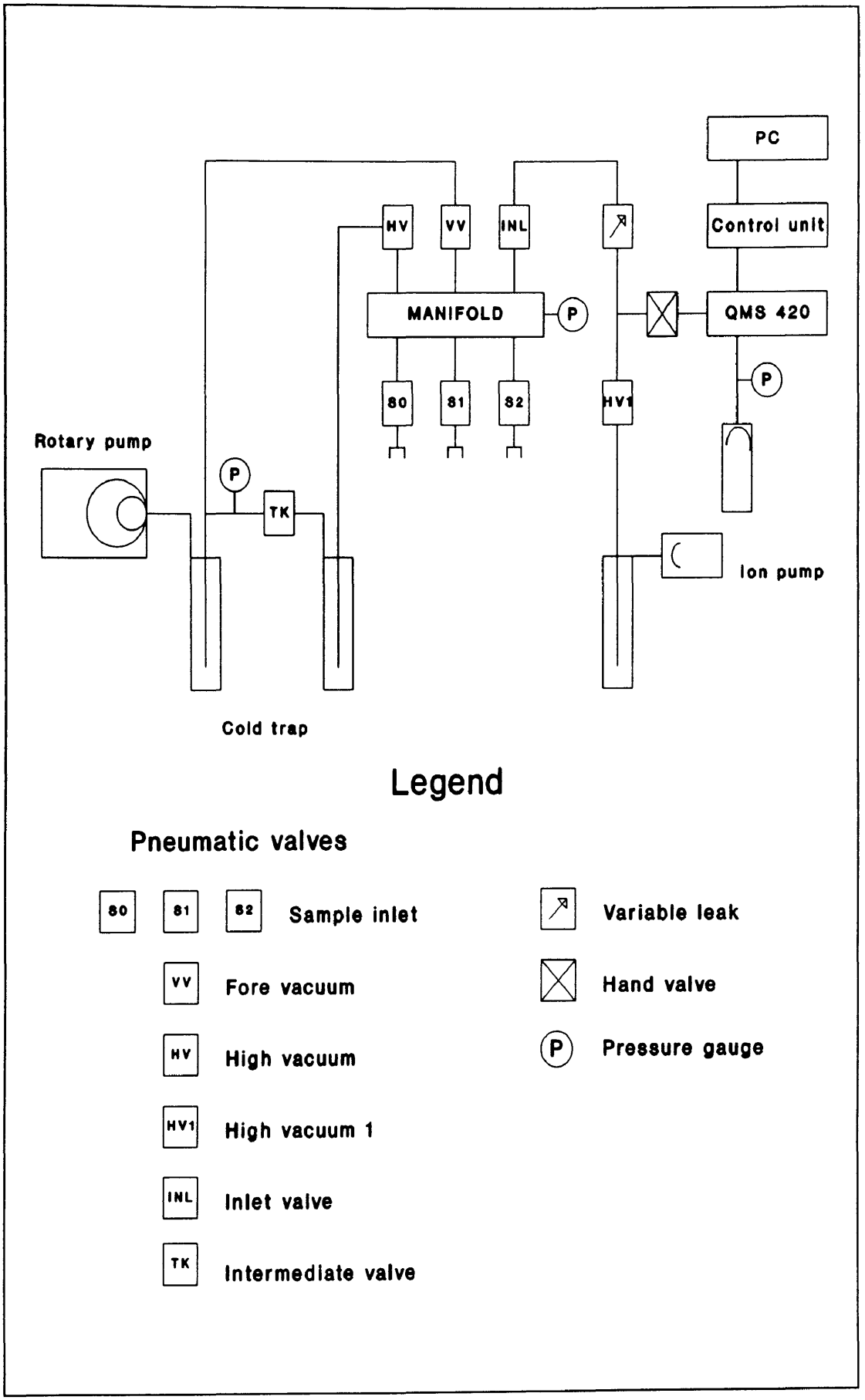


Figure 3.1 Schematic diagram of the apparatus

the ion source[21].

The pressure in the ion source is made up of the sum of the system background pressure and the pressure created by the sample. Background partial pressures may originate from degassing from the chamber walls, from components in the vacuum system, reactions of residual material on hot filaments, back flow and/or gas release in the ion pump, or from exchange reactions at the walls due to the introduced sample gas. The precision by which a sample gas can be analysed, depends to a large extent on how well such background effects can be controlled and minimised. The simplest approach to estimate these effects, is to record a mass spectrum with the gas inlet closed and then to subtract this spectrum from that measured with an open inlet. The partial pressures measured in this way for the gases present are, however, generally different from the partial pressures after the introduction of the sample. Exchange reactions on surfaces in the inlet system and ion source chamber may change the background gas composition. For many gases, particularly those of polar and reactive nature, these effects may be large and the simple background subtraction method would be unreliable. A common method to overcome this problem is by passivation of the surfaces that come in contact with the sample gas.

Corrosive gases such as UF_6, F_2 and HF are extremely reactive and special problems such as surface adsorption arise when these gases are injected into the mass analyser. Surface reaction problems can be largely avoided by conditioning metal surfaces with a thin film of fluoride and by using an ion source and analyser which is as open as possible[22], the latter thus facilitating high pumping speed to remove residual UF_6 between analyses.

The fundamentals of ion separation have been discussed in section 2.2. The separated ions are detected electrically by either a Faraday collector, or a 90° off-axis secondary electron multiplier (SEM) system. In the Faraday collector, ions strike a collector and give up their charge, thereby producing an electric current which can be measured. If the ion currents are very small, or very fast measuring times are required, a secondary electron multiplier is used as an additional amplification element. The ions to be detected are accelerated onto the first conversion dynode which amplifies the current by releasing a number of electrons. These are accelerated further onto a second and further dynodes, thereby producing an amplification typically in the order of a thousand-fold.

A cross beam electron impact (EI) ion source is used to ionise the gases in the Balzer's QMS 420 quadrupole. This instrument can analyse masses up to 512 Daltons with a peak width of one Dalton. Both detectors can analyse ions with a dynamic range of five orders of magnitude. If the typical SEM gain of a thousand is taken into consideration, the total dynamic range that the instrument can measure spans eight orders of magnitude. The control unit controls all the functions of the quadrupole, including analog to digital conversion of signals and can be programmed via the RS-232-C interface. When the corresponding mnemonics are transmitted, the computer can control the quadrupole control unit, transmit functions and acquire data. Communication is via a buffer which can temporarily store input and output transmissions. Communication syntax between the control unit and the PC must be set for a 9600 baud rate, no parity, eight data bits and one stop bit using twisted data cables between the RX and DX inputs.

The PC used was a 640K EGA XT machine with two serial ports and

one printer port. A faster computer would give no additional benefits as the critical time factor is the analysis time. Printing time is minimised by printing during the following analysis, while the PC is waiting for the ion source pressure to stabilise.

3.2 Computer program for the deconvolution of mass spectra and quantification of impurities

3.2.1 Gauss-Seidel deconvolution procedure

A mass spectrum can be composed of many fragment ions. Peak heights of a compound with such multiple fragments are proportional to the ion abundance of the fragment, i.e. peak height of a fragment divided by the ion abundance of that fragment, should be constant for each fragment. However, if there are other impurities present, the mass spectrum for one compound could overlap with that of another causing the peak height of the overlapped areas to be higher than the peak height of the compound on its own. As the peak height of that fragment contains contributions from other compounds, the ratio of the peak height over the concentration of species under examination will be higher. Consequently, the lowest ratio will have the least amount of impurities and can be assumed to be equivalent to a relative peak height of one.

As mentioned in section 2.3, the Gauss-Seidel iteration method is used to determine the intensities for each component. This method is far more efficient than a matrix method which requires more data manipulation to obtain a triangular matrix. Although there are advantages to using this method it appears that most, if not all, mass spectrometry software use a matrix reduction routine. The computer program first calculates the lowest ratio for the two most abundant fragments, then it uses this ratio as the initial estimate for the iteration procedure. The new value obtained is checked to confirm whether it is within the allowed range, (zero $\leq$ value $\geq$ lowest ratio), and corrected if it is out of range. This sequence is repeated ten times, each time refining the result.

The iterative method can best be explained by an example using a hypothetical mixture of propane, carbon dioxide, ethylene and carbon monoxide. Individual abundances of ions of the (known) constituents of the mixture are given as ion counts at the base peaks listed below.

	C_3H_8	CO_2	C_2H_4	CO	
Abundance	603	812	2129	775	
at m/e	29	44	28	28	
Giving rise to the following mass spectrum					
m/e	Peak height				Total
12	3.0	49.5	40.5	32.6	125.5
14	16.9	0	125.6	5.4	147.9
27	270.0	0	1360	0	1630
28	354.6	71.5	2129	775.0	3330
29	603.0	0.8	46.8	9.3	659.9
41	80.8	0	0	0	80.8
43	135.7	0	0	0	135.7
44	151.4	812.0	0	0	963.4
The normalised fragmentation pattern of each compound is					
12	0.5	6.1	1.9	4.2	
14	2.8		5.9	0.7	
27	44.7		63.9		
28	58.8	8.8	100	100	
29	100	0.1	2.2	1.2	
41	13.4				
43	22.5				
44	25.1	100			

The two most abundant peaks M1 and M2 are selected from each spectrum that potentially contributes to the total mass spectrum. This ensures a strong diagonal dominance in the matrix and enables the iteration process to converge to the result[23].

	C_3H_8	CO_2	C_2H_4	CO
M1	29	44	**28**	**28**
M2	28	28	27	12

There is an overlap on M1 for C_2H_4 and CO, therefore examine abundances of M2: 63.9 and 4.2. As the abundance of M2 for C_2H_4 is highest, swop M1 and M2 for C_2H_4. Therefore

	C_3H_8	CO_2	C_2H_4	CO
M1	29	44	**27**	28
M2	28	28	**28**	12

As can be seen, M1 is unique for each compound and is now used to separate the spectrum by a series of equations.

$$P_{[M]} = \sum_{i=1}^{n} A_{[i,m]} \cdot X_{[i]}$$

$$\therefore X_{[i]} = \frac{P_{[M]} - \sum_{j=1}^{n,\, j \neq i} A_{[j,m]} \cdot X_{[j]}}{A_{[i,m]}} \quad where \qquad (4)$$

$P_{[M]}$ = *Total peak height at mass m*

$A_{[i,m]}$ = *Relative abundance of compound i at mass m*

$X_{[i]}$ = *Amount of compound i*

The following four equations can be compiled:

$X(C_3H_8) = (P(29) - 0.1\ X(CO_2) - 2.22\ X(C_2H_4) - 1.2\ X(CO))/100$

$X(CO_2) = (P(44) - 25.1\ X(C_3H_8))\ /\ 100$

$X(C_2H_4) = (P(27) - 44.7\ X(C_3H_8))\ /\ 63.9$

$X(CO) = (P(28) - 58.8\ X(C_3H_8) - 8.8\ X(CO_2) - 100\ X(C_2H_4))/100$

	C_3H_8	CO_2	C_2H_4	CO
An initial estimate is made using the peak height at M1 and M2				
P[M1]/A[i,M1]	6.6	9.6	25.5	33.3
P[M2]/A[i,M2]	56.6	378.4	33.3	29.9
Select minimum	6.6	9.6	25.5	29.9
U[0]	6.600	9.634	25.50	29.89
The new value is inserted at each step (underlined)				
Solve for C_3H_8	**5.670**	9.634	25.50	29.89
Solve for CO_2	5.670	**8.210**	25.50	29.89
Solve for C_2H_4	5.670	8.210	**21.54**	29.89
Solve for CO	5.670	8.210	21.54	**7.702**
Therefore U[1]	5.670	8.210	21.54	7.702
The iteration process is repeated to converge to the final result:				
U[2]	6.025	8.121	21.29	7.749
U[3]	6.030	8.120	21.29	7.750
U[4]	6.030	8.120	21.29	7.750
Using the iteration results the deconvoluted base peaks abundances are determined exactly as chosen in the example				
	603.0	812.0	2129	775.0

3.2.2 Concentration determination with internal standards

The UF_6 can be used as an internal standard, where the unknown signals are compared to the UF_6 signals and using the relative response factors, the concentrations can be determined. The precision is improved due to the fact that UF_6 undergoes multiple fragmentation, resulting in approximately 30 large stable peaks in the spectrum (Figure 2.1), each of which can be used as an independent internal standard. As the precision is inversely related to the square root of the number of observations, the more peaks used as a standard, the better the precision of the method will be.

In order to match the mass and ionisation potential, the UF_x^{2+} ions were selected in this investigation as they cover a wide mass range of interest and their signal strength closely matches that of the analytes. The UF_x^{2+} peaks were selected in preference to the UF_x^{3+} peaks, which are closer to the analytes masses, but which were rejected because of their greater peak instabilities. All five UF_x^{2+} peaks were used for the analyses but only the UF^{2+} peak was used in the validation of the method.

Fluctuation in the total ion yield and transmission affects both the UF_6 peaks and the unknown compound mass spectra, but the relative response factors remain constant within the framework of ion statistics. After a major service to the mass spectrometer, the relative response factor should be redetermined. Minor changes in RRF can be ascribed to changes in the transmission probabilities of different masses as conditions inside the mass spectrometer change (see 2.4).

The method can be expanded to include other trace impurities by characterising and measuring the unknown spectrum and calculating the

relative response factors. These data are then entered into the data file and the computer will calculate the concentrations. Any sample which is primarily a pure compound containing only trace impurities can be analysed using this method. With minor modifications to the program the method may be adapted for on-line measurements for quality control purposes in a variety of industrial applications.

Firstly, the two most intense peaks in the mass spectrum of each of the known constituents are entered for each compound . The iteration is then performed to elucidate the contribution of the base peak for each compound as shown in section 2.4. The computer program subsequently uses the intensities of the impurity peaks calculated, and divides these by the intensity of the selected UF_6 peaks and the stored RRF values, to obtain the concentration of each impurity relative to UF_6. As shown in Figure 2.1, the UF_6 fragments into approximately 30 large stable peaks. Of these, the doubly charged fragments, $^{235}UF_x^{2+}$, are used as internal standards for reasons discussed above.

As shown in section 2:4, *equation* 3: $$\frac{[i]}{[UF_6]} = \frac{I_i}{I_{UF_6}\, RRF_i}$$

This procedure treats the $^{235}UF_x^{2+}$ fragments as a quantitatively fixed feature of the UF_6 mass spectrum. Clearly an appropriate correction has to be made when the ^{235}U isotope abundance deviates from the 0.727% of natural uranium. The concentration ratio, [i] / [UF_6], is often expressed in parts per million (ppm), mole per mole UF_6. This figure also reflects the mole/mole sample concentration of a particular impurity, provided that there are no major impurities in the UF_6.

3.2.3 The Pascal program "SCAN"

The SCAN program is a self-contained application software package written in Turbo Pascal, that enables the user to control measurement parameters, acquire data and efficiently determine the concentrations of trace impurities in a matrix, with minimum operating commands. The writing of this program was an integral part of the thesis and all original source code is therefore reproduced in the appendix.

SCAN uses an eight peak spectrum library of components and peak intensity data. This spectrum library can be easily modified to include a larger array of compounds. During data acquisition, the intensities at preselected masses are recorded with an automatic adjust and auto-range procedure. Due to the low concentrations measured, (less than 10 ppm), extreme care is needed in the measurements. The blank measurements must be subtracted prior to data processing.

To determine the intensities, equation 4, section 3.2.1 is used. By the repeated application of only this one equation, the weighted contribution of each target compound spectra is determined. The coefficients of the matrix, A[i,m], are stored in an array according to the mass. The position of A[i,m] in this array is stored in column i, row 2m, (the row is doubled because half masses are used). Because the data are stored according to mass, the coefficient can be obtained directly without having to use a sorting procedure which would first have to retrieve the mass and if the mass was correct, to then retrieve the coefficient. Although the array contains mostly zero's and is therefore not memory conservative, it is the speed of access which is important.

The weighted contribution of the spectrum of each target compound calculated, is used with the response factors of each component relative

to the sample matrix (internal standard), to calculate the concentration of the trace impurity.

An automatic reporting facility is available for printing of the results. As this method is designed to handle large sample batches, all of the results are stored in a single file. Approximately 500 analysis results can be stored on a single 360k byte floppy disk. The program was designed for fast, accurate analysis of low concentrations, with the minimum of operator supervision. Consequently, the operating parameters of the quadrupole mass spectrometer are preset on the quadrupole control unit, and only the measurement parameters are computer controlled. In line with the philosophy of minimum operator intervention, there are only two menu's, one of which is seldom used. These are described in the next section.

3.2.4 SCAN program functions

An overview of the main program functions is given in Tables 3.1 and 3.2 which list both menus, with brief comments on what each menu option does.

Table 3.1 Main menu

0 - Scan the mass range	Type in the sample data Measure intensities Background subtraction Resolve the spectrum Determine concentrations Save results to file Print report
1 - Modify parameters	Modify menu
2 - Import data	Use a QUADSTAR ASCII file
3 - Printer is ON/OFF	Automatic printing of results Toggle auto-print on/off
4 - Adjust RRFs	Enter the sample record number Enter the true concentrations Calibration factors are determined Uses an averaging technique to eliminate standard error Prompt to accept if > 20% difference Update calibration file
5 - Exit SCAN	Terminate the program Exit to DOS

Table 3.2 Modify menu

0 - Modify masses	Select mass table to be scanned (10 sets) Option to change mass table
1 - View data files	View RRFs and 8-peak index
2 - Adjust data files	Enter compound to be added or changed Enter 8-peak index data
3 - View analysis files	Enter the record to be viewed View stored results
4 - Modify headings	Modify report headings per client
5 - Calculate RRFs	Calculate average RRFs using standard series
6 - Tabulate all results	Summary of stored results
7 - Adjust printout table	Select compounds to be printed on the report according to client's specifications
8 - Return to main menu	Return to main menu

3.3 Mass spectrometry operating conditions

The quadrupole mass spectrometer was used under normal routine operating conditions, except for the electron energy, which was set according to the maximum UF_6 signal at m/e 119. The instrument was only re-focused when it became necessary due to poor peak shape, lack of response or poor precision of control samples. Typical ion source and scan parameters are given in Table 3.3. Reference 24 describes each of these terms and the focusing procedure.

Table 3.3 Typical ion source and scan parameters

ION SOURCE PARAMETERS		SCAN PARAMETERS	
Emission	1.00 mA	Channel	0
Protection	4.70 V	Ch-mode	SAMP-N, PEAK-F
Ion reference	102 V	First mass	Program selects
Cathode	92.00 V	Width	1 Dalton
Focus	15.25 V	Speed	0.1s and 2s
Field axis	19.00 V	Resolution	10
Extraction	180 V	Range	E-05 to E-12
Deflection	262 V	Detector	SEM, FARADAY
		Filter	AUTO
		Sem	1600 TO 1900 V
		Offset	0.00 V
		Calman	1.00
		Threshold	100 mV

3.4 Initialisation of data files

There are two data files required for the analysis. These are the data file containing the masses to be scanned, and the file containing the relative peak intensity of the eight most abundant peaks for each compound of interest. These two files are only changed if the list of target compounds to be analysed changes. An eight peak data index file for the compounds of interest was created using literature information. Not all compounds have a complete eight peak index. The reasons for this being:

- fewer than eight peaks occur in a spectrum;
- other peaks may not be relevant to the calculations since those masses are not significant and are therefore not scanned.

The program requires at least two peaks per compound. If there is only one significant peak for a compound, the program requires that the first peak be duplicated (see N_2 in Table 3.4). The order of the first two peaks in the data file is important and must be set to the two most significant peaks in the spectrum. The order of the other six peaks in the index file is irrelevant, as they are only required for the determination of contributing factors to the peak heights, at the significant masses for each of the other compounds (refer to equation 4, section 3.2.1).

Only relative peak heights are required in the index file. Therefore the fragments can be normalised to the base peak of the compound, or the sum of the fragments can be equal to 100 %, or the fragments can be normalised according to isotopic peaks. The four most abundant fragments are shown in an abridged eight peak data index file in Table 3.4. From this index file, the masses to be scanned were selected, according to the two most unique masses per target compound, as is shown in Table 3.5.

Table 3.4 Abridged data file showing four most abundant fragments

Compound	m/e	Int	m/e	Int	m/e	Int	m/e	Int
CF_4	69	100	70	1.1				
Cl_2	72	37	70	57	74	6		
$Cr_2O_2F_2$	122	47	52	39	71	26	103	19
F_2	38	100	38	100				
Freon-11	101	57	103	37				
Freon-113	151	100	153	64	101	23	69	11
N_2	28	100	28	100				
O_2	32	100	32	100				
PF_5	107	100	88	4	69	4	50	5
SF_6	89	100	108	36	70	30	72	1.3
SO_2F_2	83	100	102	74	67	29		

Table 3.5. Table of masses to be scanned

Compound	Mass	Compound	Mass	Ion	mass
N_2	28	SF_6	89	UF^{2+}	117.5
O_2	32	Freon-11	101	UF_2^{2+}	127.0
F_2	38	SO_2F_2	102	UF_3^{2+}	136.5
$Cr_2O_2F_2$	52	Freon-11	103	UF_4^{2+}	146.0
CF_4	69	PF_5	107	UF_5^{2+}	155.5
Cl_2	70	SF_6	108		
Cl_2	72	$Cr_2O_2F_2$	122		
SO_2F_2	83	Freon-113	151		
PF_5	88	Freon-113	153		

3.5 Sample and standard preparation

No sample preparation is required by the mass spectrometrist. Possible problems that might occur during sampling are due to poor evacuation of the sample container and/or manifold, and non-homogeneity of the sample, especially when the sample is in two phases, eg a gas/solid phase of UF_6.

Gas standards are required for calibration purposes for a large variety of gas compositions. A gas transfer apparatus is used for this purpose, the operation of which is based on the principles of ideal gases, which allows the synthesis of the required standards. In this method, gas is introduced into a vessel of known volume to a specific pressure. This is then allowed to expand into a second known volume filled with a second gas. An intermediate valve is opened and the gases mix by diffusion. Using Boyle's law, the gas composition can be determined according to the partial pressures of each gas.

$$P_i V_i = n_i RT$$

where:

- P_i is the pressure of gas i;
- V_i is the volume of the vessel containing gas i;
- n_i is the number of moles of gas i;
- R is the gas constant = 8.314 J K^{-1} mol^{-1};
- T is the temperature in Kelvin which is held constant;

$$\textit{Rearranging yields } n_1 = \frac{P_1 V_1}{RT} \quad \textit{and} \quad n_2 = \frac{P_2 V_2}{RT}$$

For a binary mixture the total amount of moles = $n_t = n_1 + n_2$

$$\textit{The concentration of gas } 1 = C_1 = \frac{n_1}{n_t}$$

$$\textit{therefore } C_1 = \frac{\frac{P_1V_1}{RT}}{\frac{P_1V_1}{RT} + \frac{P_2V_2}{RT}}$$

$$\textit{RT cancels out leaving } C_1 = \frac{P_1V_1}{P_1V_1 + P_2V_2}$$

3.6 Analysis Procedure

Gas sampling vessels are connected to one of the three inlets as shown in Figure 3.1. Air is evacuated using VV, and when the pressure gauge has stabilised the system is further evacuated using HV.

From the menu selections, option zero is chosen, "*scan the mass range*". The program first requests the sample information, after which the sample is let into the inlet system and the sample pressure is recorded from the Validyne pressure gauge. The sample is then let into the instrument and the inlet pressure is recorded. A delay time of three minutes is allowed for the source pressure to stabilise, after which selected ions are monitored according to the mass table selected.

The spectrum measurement sequence is fully computer controlled. Using the preselected mass table, selected ions are monitored. For each mass of interest, the signal range is determined during a fast (0.1s) auto-range sequence, where the signal is adjusted to between 0.5 and 70 per cent of full scale. The autorange begins at the range last used for a mass. In most cases this means that the range is correct immediately and that no further range adjustments are needed. The

peak centre is then more accurately determined with a second fast scan (0.1s) with a scan width of 1 Dalton over the mass of interest. A peak finding routine in the quadrupole control unit determines the precise peak centre. The intensity at this peak centre is then monitored for 2 seconds and an integrated signal is recorded.

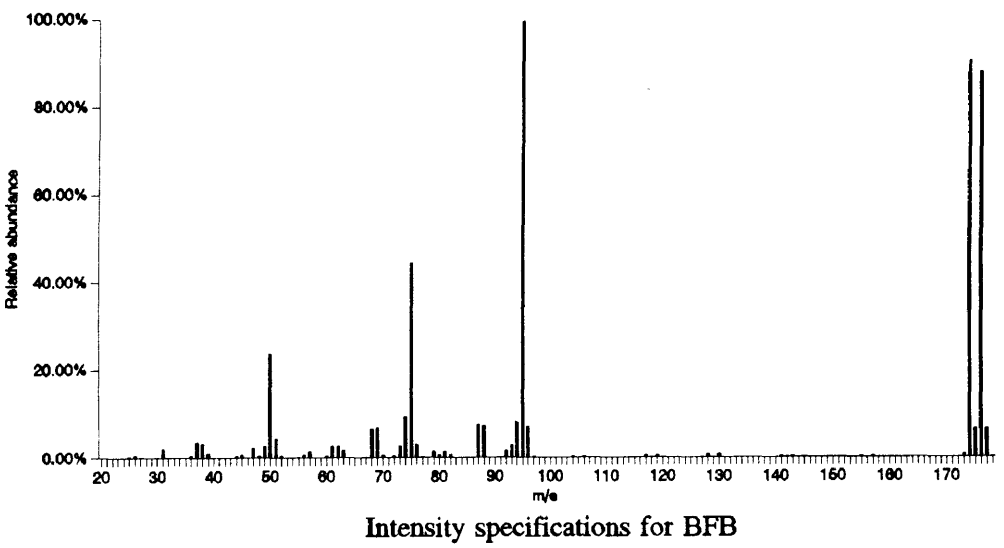
The concentrations of analyte impurities measured for each sample are calculated in the following manner:

1) All masses are rounded off to the nearest half mass. This then allows a measuring error of 0.25 Daltons on either side of the mass. Problems can arise with triply and higher charged fragments which can be rounded off incorrectly, e.g. U^{3+} at 79.3 Daltons could easily be rounded up or down and would not be recognised as the correct fragment. Fortunately, the impurities can be analysed according to singly charged fragments and this possible problem can be avoided.
2) All raw ion counts are blank subtracted using the peak intensities measured at the start of the sample batch using a blank UF_6 sample.
3) Overlapping spectra are deconvoluted by the Gauss-Seidel iteration process.
4) Concentrations are determined using relative response factors or, conversely, if the concentration is known, the RRFs are determined.

The results are recorded on the printer and saved on the hard disk.

3.7 Evaluation of the system

In organic mass spectrometry, where the analyst would expect a variety of compounds in a sample, it is vital that the instrument parameters be carefully checked. This is usually accomplished by means of a reference sample which, when analysed, has a reproducible mass spectrum over the mass range of interest[25]. The instrument must be tuned at least daily to confirm that the spectrum is within certain limits as prescribed by various regulatory bodies. Figure 3.2 shows the mass spectrum of bromofluorobenzene (BFB) and the relative intensity intervals as prescribed by the United States of America Environmental Protection Agency (EPA) for the determination of volatile organics in a variety of matrices[26].



Intensity specifications for BFB

Mass	Relative intensity	Mass	Relative intenity
50	15 to 40 % of mass 95	173	< 2 % of mass 174
75	30 to 60 % of mass 95	174	> 50 % of mass 95
95	base peak, 100%	175	5 to 9 % of mass 174
96	5 to 9 % of mass 95	176	> 95 but < 101% of mass 174
		177	5 to 9 % of mass 176

Figure 3.1 Mass spectrum of 4-Bromofluorobenzene

Routine inorganic mass spectrometry is in general less complicated, in that the range of compounds encountered in a sample is usually

significantly less than that in organic analysis, and only a selected number of compounds are analysed during each analysis. This results in less severe restrictions in the quantification of compounds in the matrix. A comprehensive computer search is not required to validate an identification. Consequently the instrument parameters need not be as carefully monitored, as is the case in quantitative organic mass spectrometry.

Apart from control samples with each batch of samples, the mass spectrometer is only checked on a weekly basis. Tuning is only performed when an error is observed, and it is not unusual if the only adjustments performed on the instrument in six months, are minor changes to the secondary electron multiplier voltage. However, it should be noted that the success or failure of the relative response method described in this thesis, is critically dependent on the stability of the internal standard peak height with respect to the peak height of other compounds present. This relies on the reproducible fragmentation of the UF_6 and transmission of the ions formed. The stability of the UF_6 peak intensities were hence investigated to determine the feasibility of the method.

Although observed fragmentation patterns can depend on ion source pressure, the design of the instrument incorporates a small variable leak which buffers any variation of inlet pressure. Thus the source pressure is mostly a function of the internal open area of the valve and consequently the fragmentation pattern is independent of sample inlet pressure. Likewise the RRFs which are dependent on the stability of the fragmentation pattern should also be independent of pressure.

The reproducibility of relative response factors was investigated with reference to both time and concentration, and compared to the external

calibration method. The method uses five UF_6 peaks as internal standards and the resulting improvement in precision was evaluated.

A number of samples were received where the U isotope composition of the UF_6 was not natural. Measurements were taken to quantify the effect of isotopic composition on uncorrected results, obtained from the standard procedure that presupposes 0.727% ^{235}U composition. Detection limits for the method were evaluated using blank concentrations for each target compound.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Reproducibility of relative peak intensities of the UF_6 mass spectrum

Data acquired over two years, showed significant fluctuation of the UF_6 peak heights (Figure 4.1). The peak heights plotted are those of $^{235}UF^{2+}$ at m/e 126,5. On careful examination of the data it can be observed that there was a gradual loss of response as the instrument became contaminated, followed by a sharp rise in peak heights after the instrument was cleaned.

The relative response method overcomes the problem of the fluctuation of instrument response over time by measuring relative peak heights. Therefore, to demonstrate the stability of the internal standard method, relative peak heights and not absolute values must be obtained. If the instrument parameters change, this could cause some mass discrimination at either the low or high mass end of the spectrum, resulting in changes of relative peak heights.

The data were used to plot the UF_x^{2+} peaks relative to the UF^+ peak (Figure 4.2). The data were grouped into service intervals, and from Table 4.1 it can be seen that during a particular service interval the relative peak heights fluctuated by 4 %, which is within the expected 5 % internal precision of the instrument. Between the intervals the relative values fluctuated by 13 %, as a result of mass discrimination effects caused by refocusing.

As the relative peak heights are far more stable than the absolute values, the relative response values remain stable over long periods of

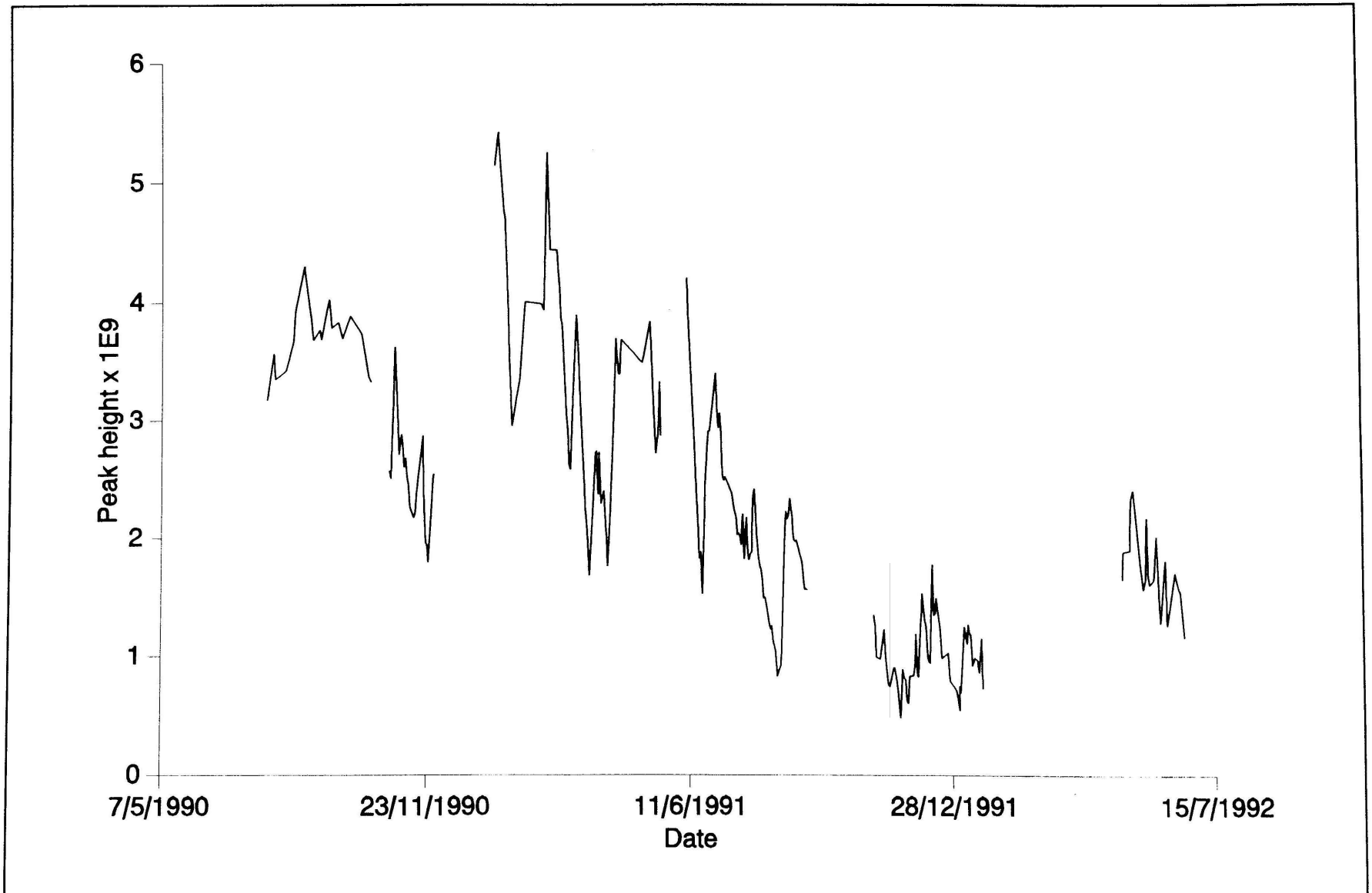


Figure 4.1 $U^{235}F^{2+}$ ion abundances

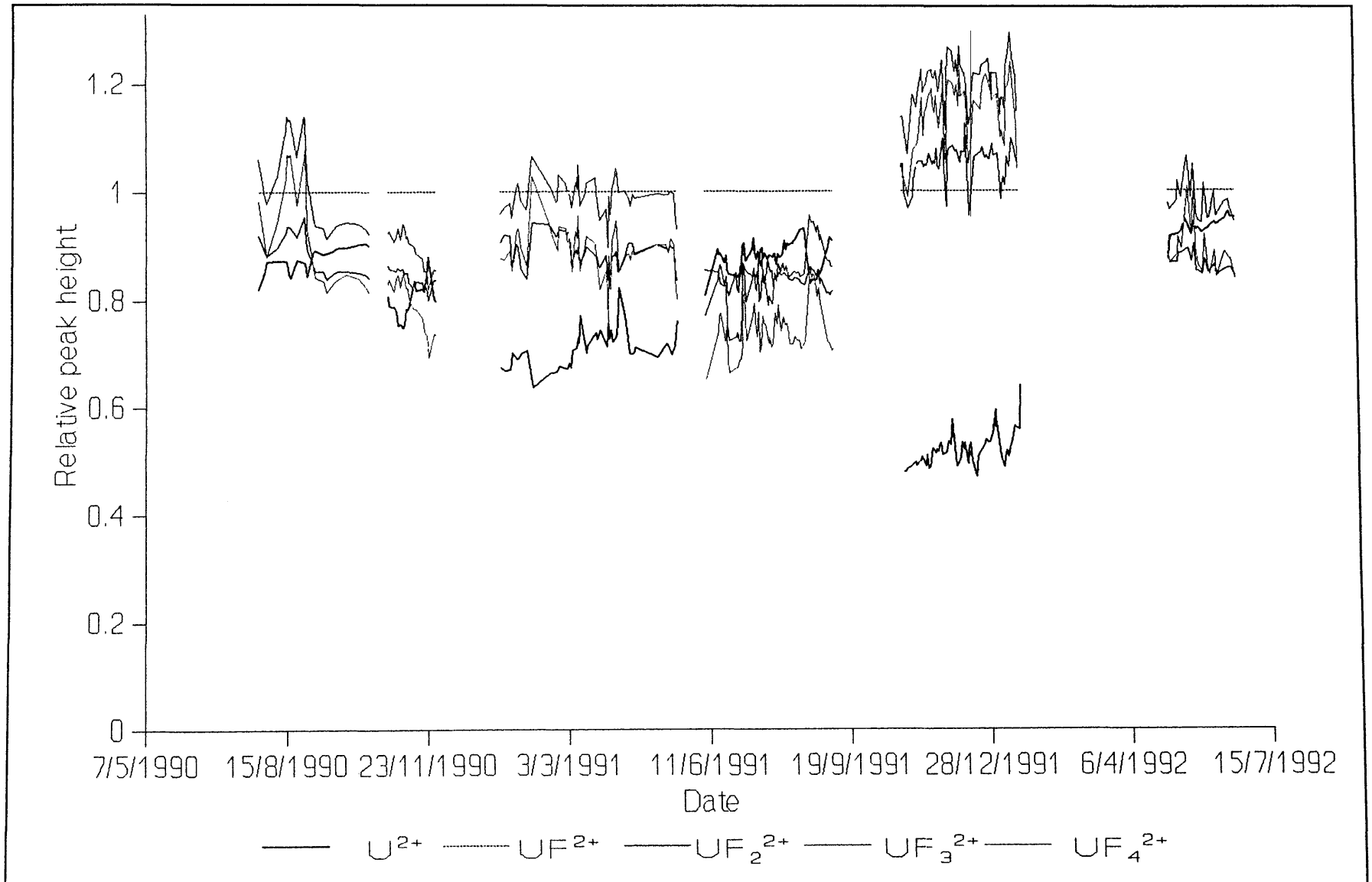


Figure 4.2 Internal standards relative to $U^{235}F^{2+}$

Table 4.1 Relative peak heights (UF_x^{2+}/UF^{2+})

	U^{2+}/UF^{2+}	UF_2^{2+}/UF^{2+}	UF_3^{2+}/UF^{2+}	UF_4^{2+}/UF^{2+}
$\bar{x}$	0.8756	0.8876	1.0134	0.9248
	0.8002	0.8406	0.8952	0.7919
	0.7090	0.8905	0.9925	0.8918
	0.8802	0.8425	0.8410	0.7447
	0.5196	1.0488	1.1991	1.1402
	0.9326	0.8667	0.9845	0.8934
s	0.0218	0.0378	0.0839	0.0969
	0.0331	0.0166	0.0334	0.0460
	0.0354	0.0270	0.0291	0.0427
	0.0268	0.0168	0.0538	0.0460
	0.0316	0.0337	0.0446	0.0581
	0.0170	0.0165	0.0341	0.0450
$\%s_1$ (Within)	2%	4%	8%	10%
	4%	2%	4%	6%
	5%	3%	3%	5%
	3%	2%	6%	6%
	6%	3%	4%	5%
	2%	2%	3%	5%
$\%s_2$ (Between)	18%	8%	11%	14%

where:

- $\bar{x}$ refers to the average relative peak heights for each of the six service intervals;
- s is the standard deviation for the service interval;
- $\%s_1$ is the relative standard deviation within a service interval;
- $\%s_2$ is the relative standard deviation between service intervals.

time, and only change significantly after a service or major change to the focusing parameters. Consequently, calibrations can be performed on a weekly basis instead of daily.

4.2 Influence of ion source pressure

The data of the previous section were used to plot the relative peak heights of the UF_6 against the sample pressure (Figure 4.3). Relative peak heights of the internal standards lie within experimental error, and can be assumed to be independent of sample pressure. Therefore, provided that the sample pressure is less than the vapour pressure of the UF_6 , (12 kPa at STP), the RRFs will be independent of pressure. At pressures higher than the vapour pressure, some of the UF_6 solidifies, which will decrease the amount of UF_6 in the gas phase relative to the other compounds. This will have an influence on the relative response factors.

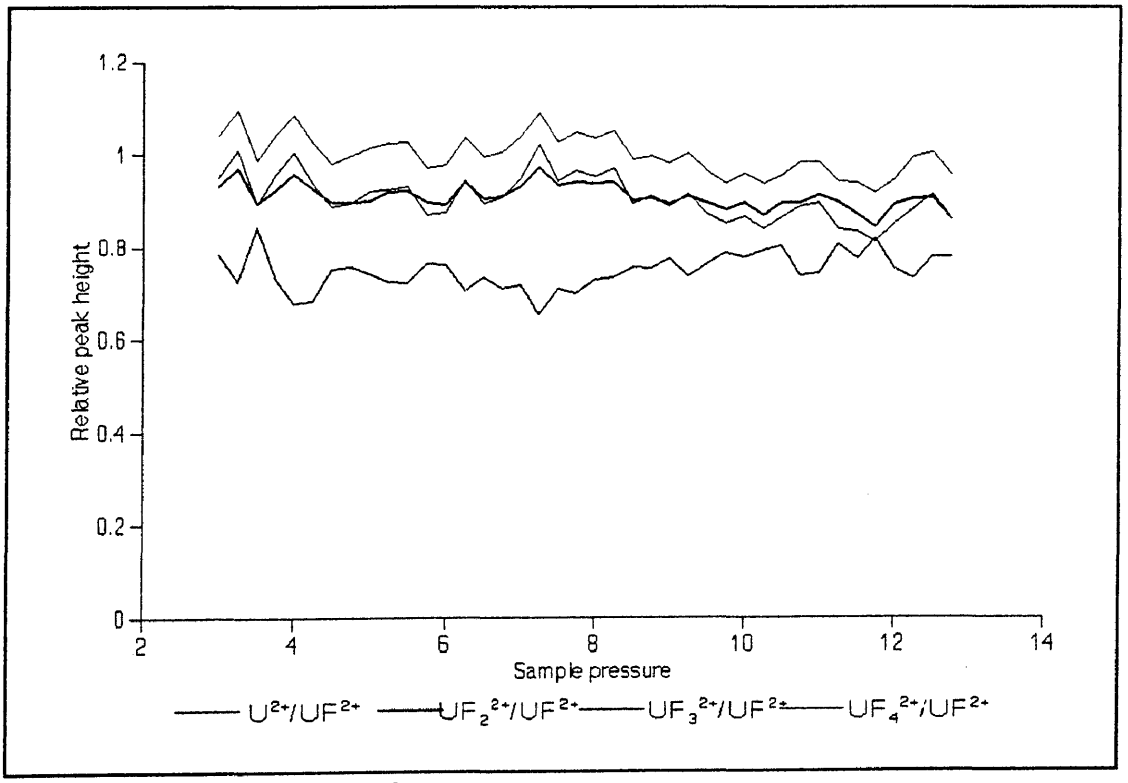


Figure 4.3 Influence of pressure

4.3 Reproducibility of relative response factors

During the time period that the data were acquired, the instrument was serviced on five occasions. The RRFs of Cl_2 and Freon-11 standards to the $^{235}UF^{2+}$ internal standard, were measured to determine the long term reproducibility of the method. These data are shown in Figure 4.4 and are summarised in Table 4.2.

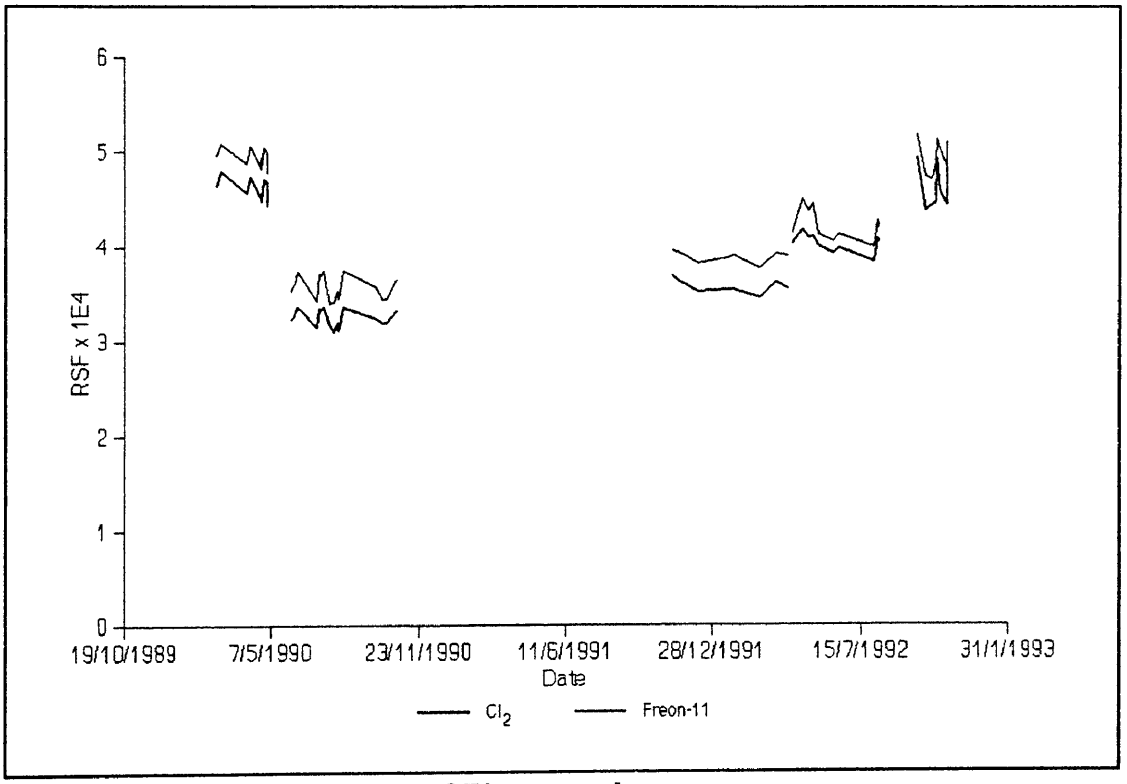


Figure 4.4 Variation in RSF's over time

Table 4.2 Reproducibility of RRFs during service intervals.

Cl_2 average	Freon-11 average	Cl_2 RSD	Freon-11 RSD
4.62E-4	4.95E-4	2.4%	2.1%
3.26E-4	3.58E-4	2.7%	3.5%
3.59E-4	3.91E-4	1.9%	1.5%
4.05E-4	4.25E-4	2.3%	3.8%
4.66E-4	4.98E-4	4.9%	3.4%

	Cl_2	Freon-11
$\bar{x}$	4.04E-4	4.33E-4
s	5.53E-5	5.57E-5
RSD	14%	13%

The data correlate well with results shown earlier, namely that during a service interval the RRFs fluctuate by less than five percent and the total precision is about fifteen percent, whereas the absolute responses fluctuate by about 25%.

4.4 Influence of concentration on accuracy

Gas standards were prepared over the normal concentration range, for all the impurities of interest, to determine if the concentration influences the RRFs. The results are shown graphically in Figures 4.5 to 4.13.

$$RRF_{is} = \frac{I_i}{I_s} \cdot \frac{[s]}{[i]} \qquad equation\ 1,\ section\ 2.4$$

$$Rearranging\ yields\ \frac{I_i}{I_s} = \frac{RRF_{is}}{[s]} \cdot [i]$$

$$Plotting\ \frac{I_i}{I_s}\ vs\ [i]\ yields\ a\ straight\ line\ with\ a\ slope\ of\ \frac{RRF_{is}}{[s]}$$

Since $[UF_6]$ is constant the RRF can be viewed as the slope of the line. Linear regression was used to evaluate the data over the concentration range. These results are listed in Table 4.3. N_2 and O_2 are measured using the Faraday and their RRFs are therefore approximately one thousand times lower. As the graphs are linear with good correlations over the concentration ranges, it can be concluded that the relative response factors for individual compounds, are independent of concentration within the concentration ranges investigated.

Table 4.3 Results of linear regression analysis.

Compound	Intercept	r	n	RRF	S_{yx}	RSD
CF_4	6.82E-5	0.9995	10	1.08E-4	8.14E-7	0.75%
F_2	-7.15E-3	0.9992	11	1.51E-5	1.39E-7	0.92%
N_2	3.27E-7	0.9997	13	7.01E-9	3.64E-11	0.52%
O_2	-1.45E-7	0.9986	12	6.06E-9	7.26E-11	1.20%
PF_5	-1.41E-5	0.9991	11	2.23E-6	2.22E-8	0.99%
SF_6	2.16E-5	0.9959	10	1.41E-5	3.21E-7	2.27%
SO_2F_2	-9.99E-6	0.9991	11	1.47E-5	1.47E-7	1.00%
Cl_2	2.85E-6	0.9952	13	3.72E-4	7.79E-6	2.09%
Freon-11	1.55E-6	0.9977	13	3.41E-4	4.92E-6	1.44%

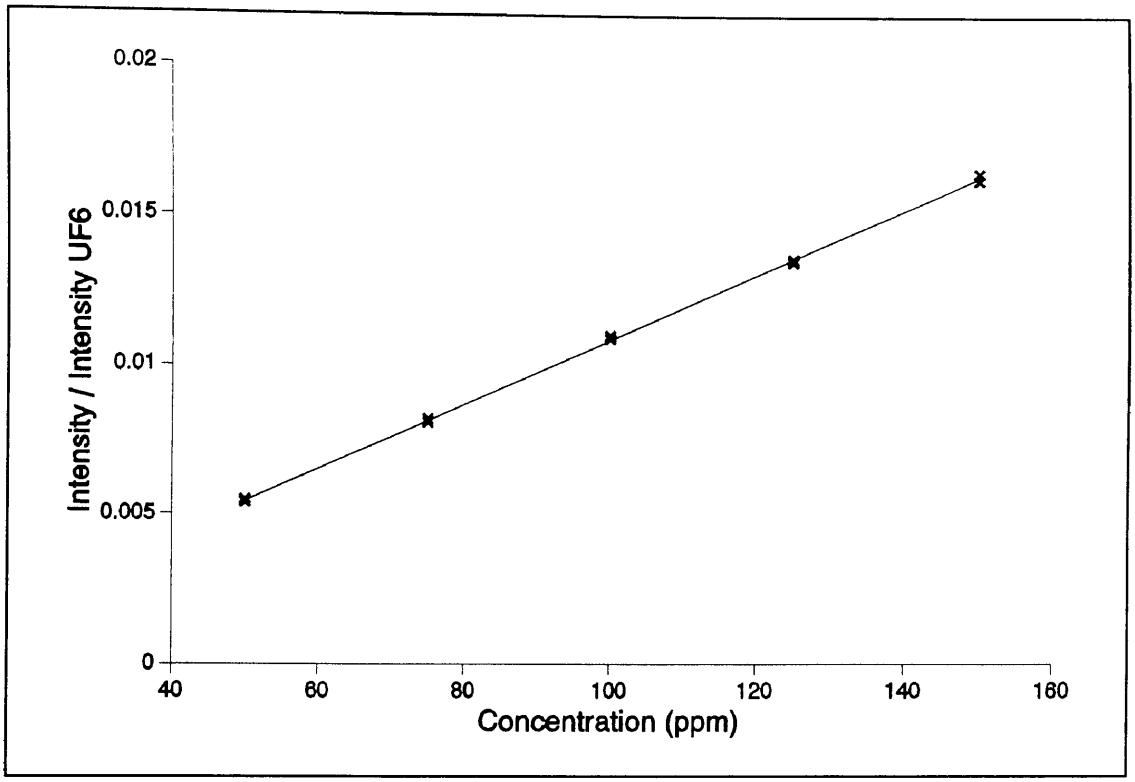


Figure 4.5 Relative response of CF_4

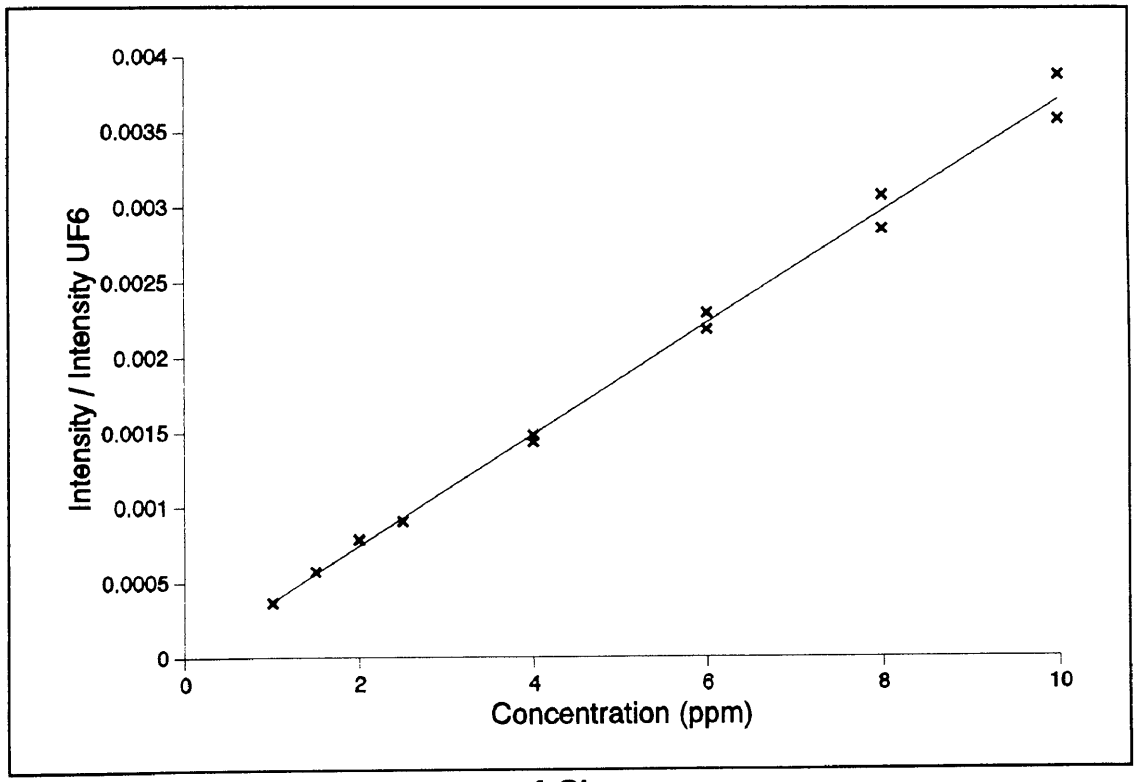


Figure 4.6 Relative response of Cl_2

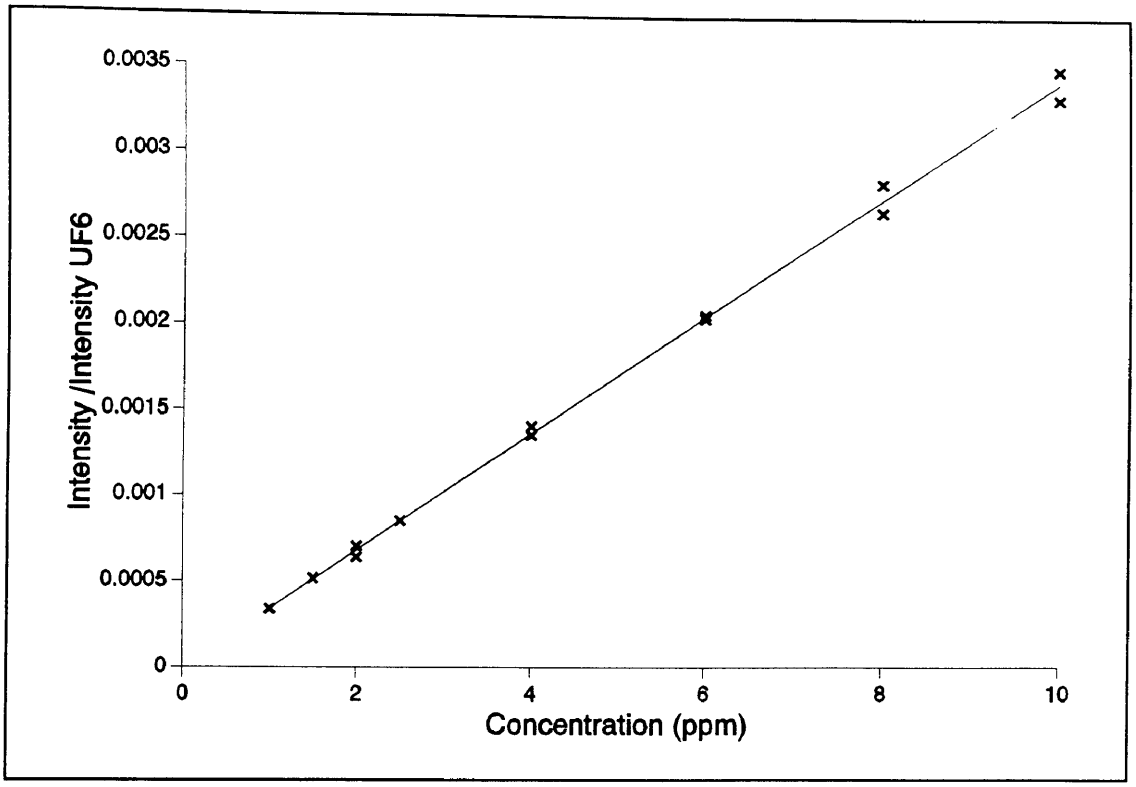


Figure 4.7 Relative response of Freon-11

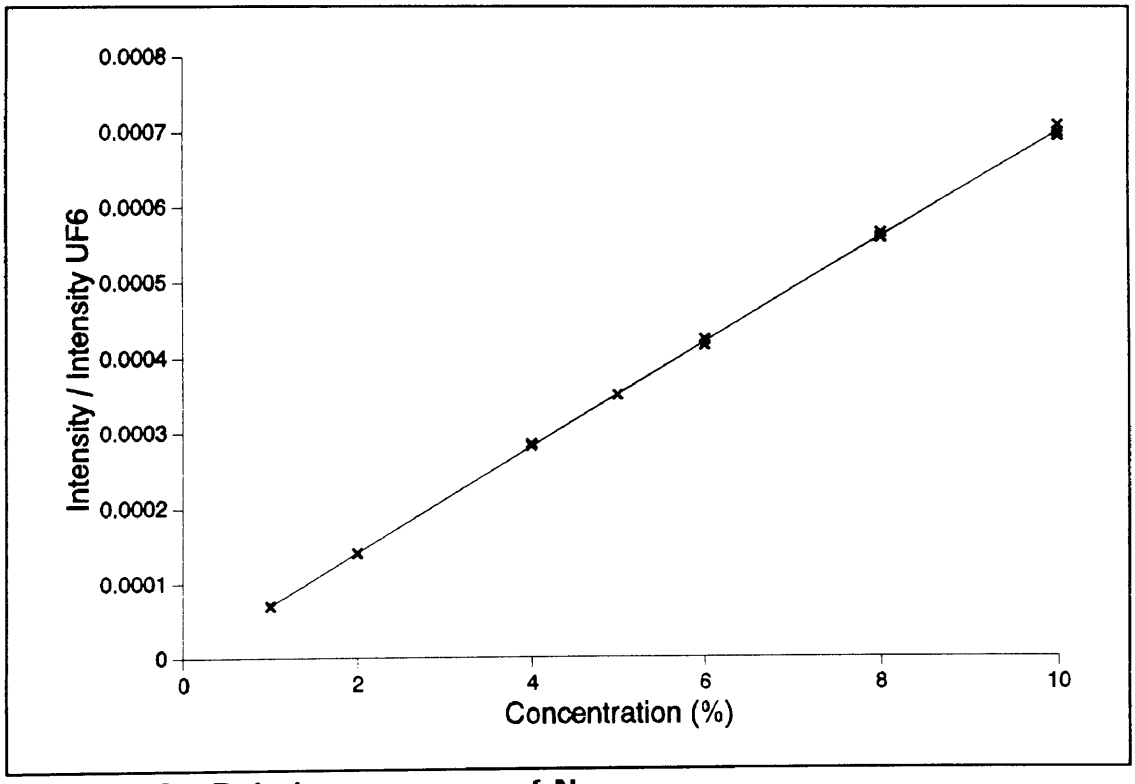


Figure 4.8 Relative response of N_2

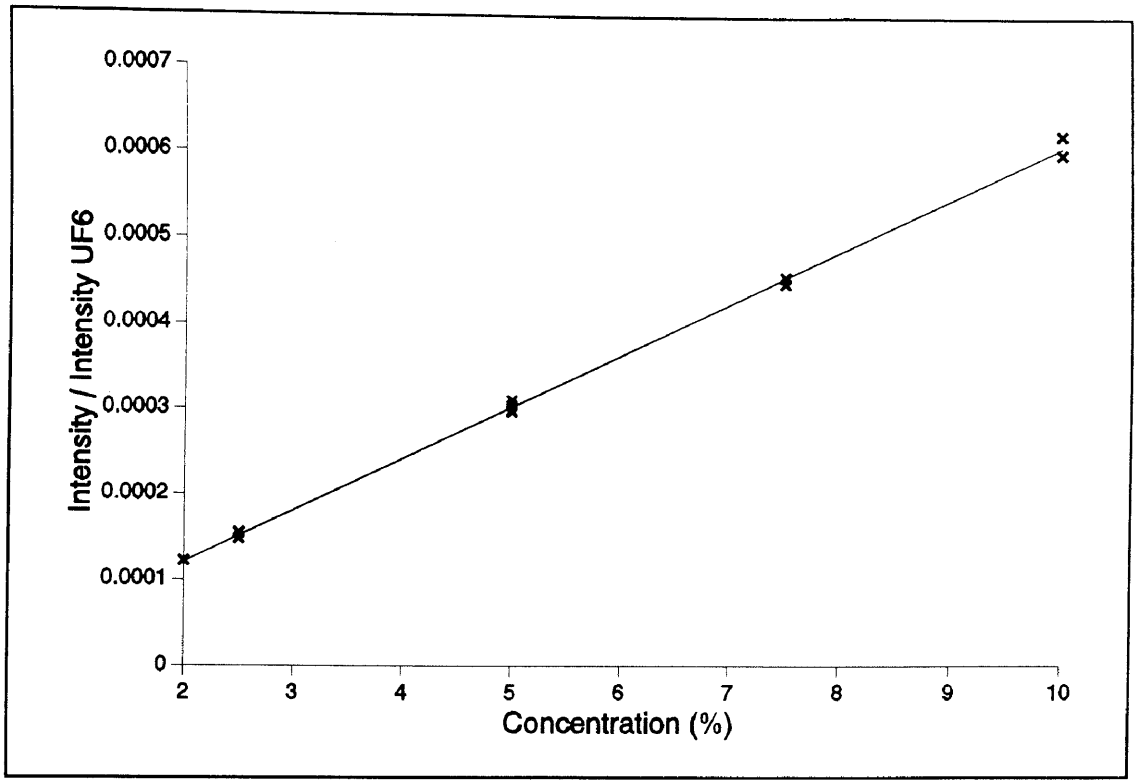


Figure 4.9 Relative response of O_2

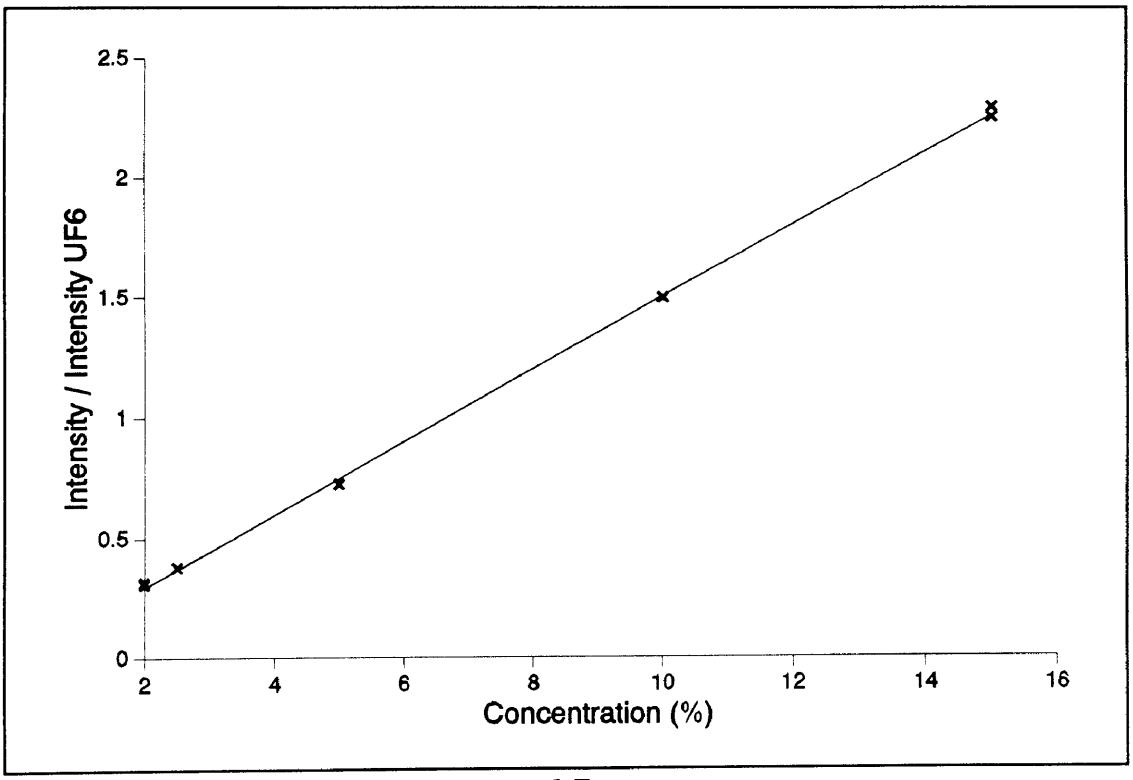


Figure 4.10 Relative response of F_2

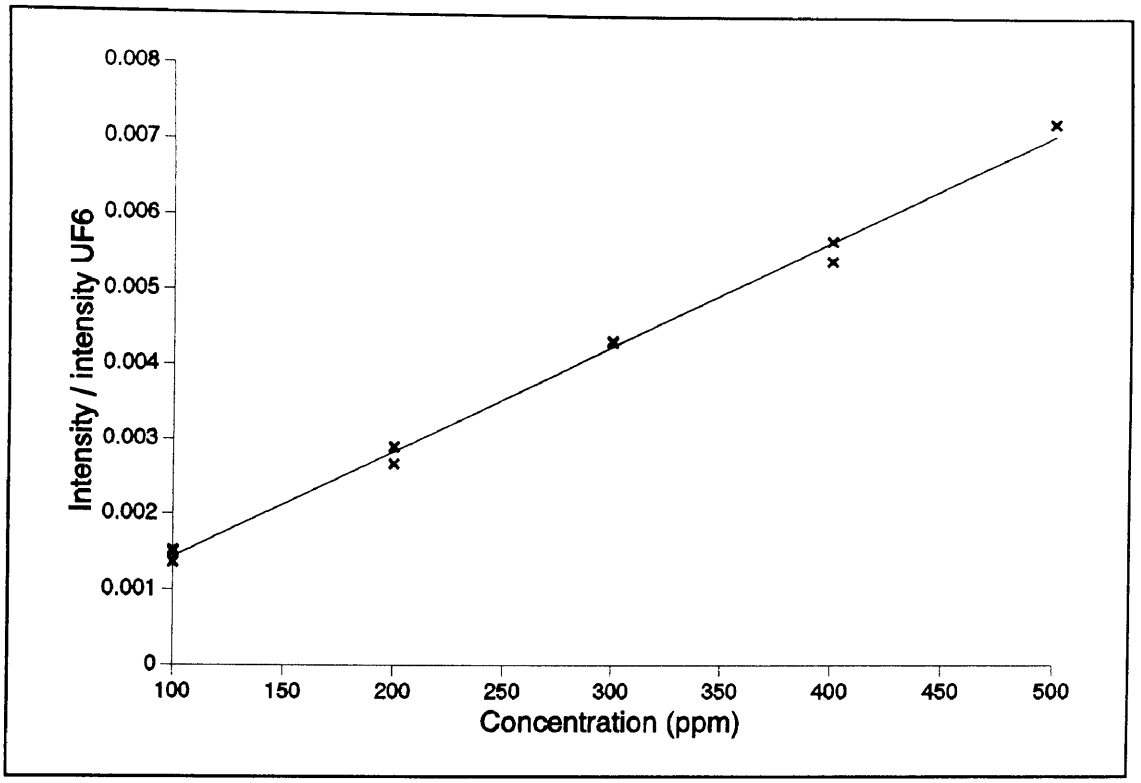


Figure 4.11 Relative response of SF_6

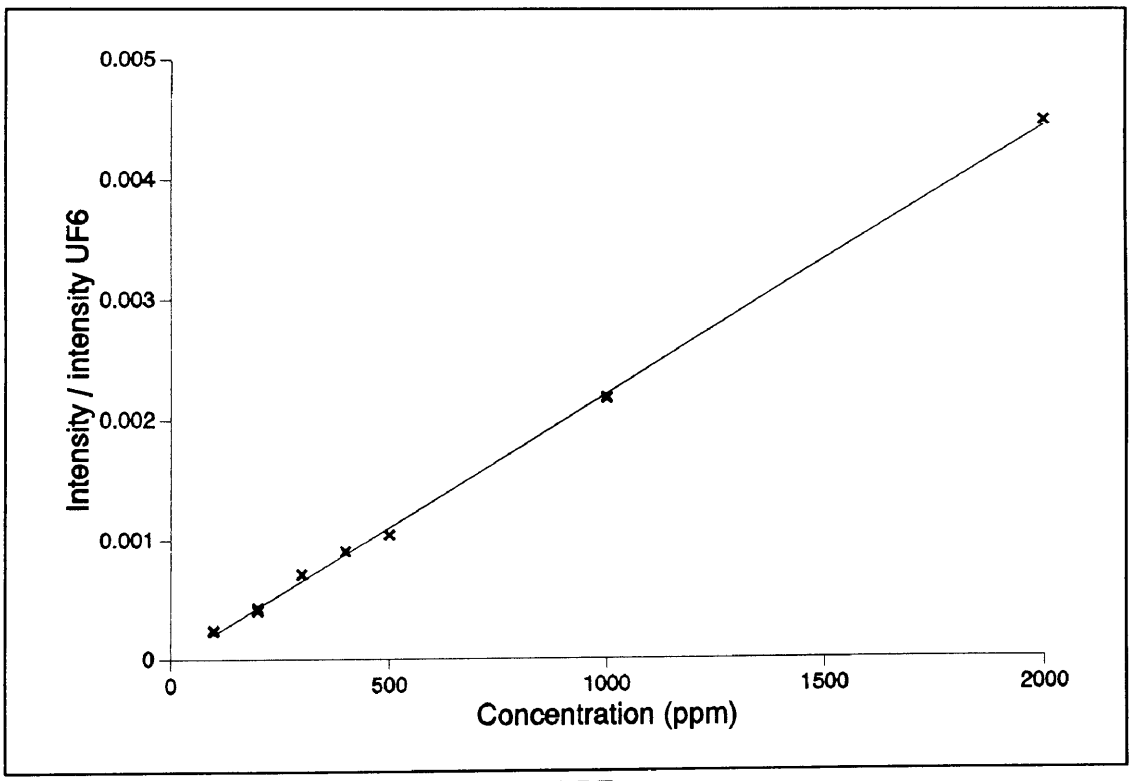


Figure 4.12 Relative response of PF_5

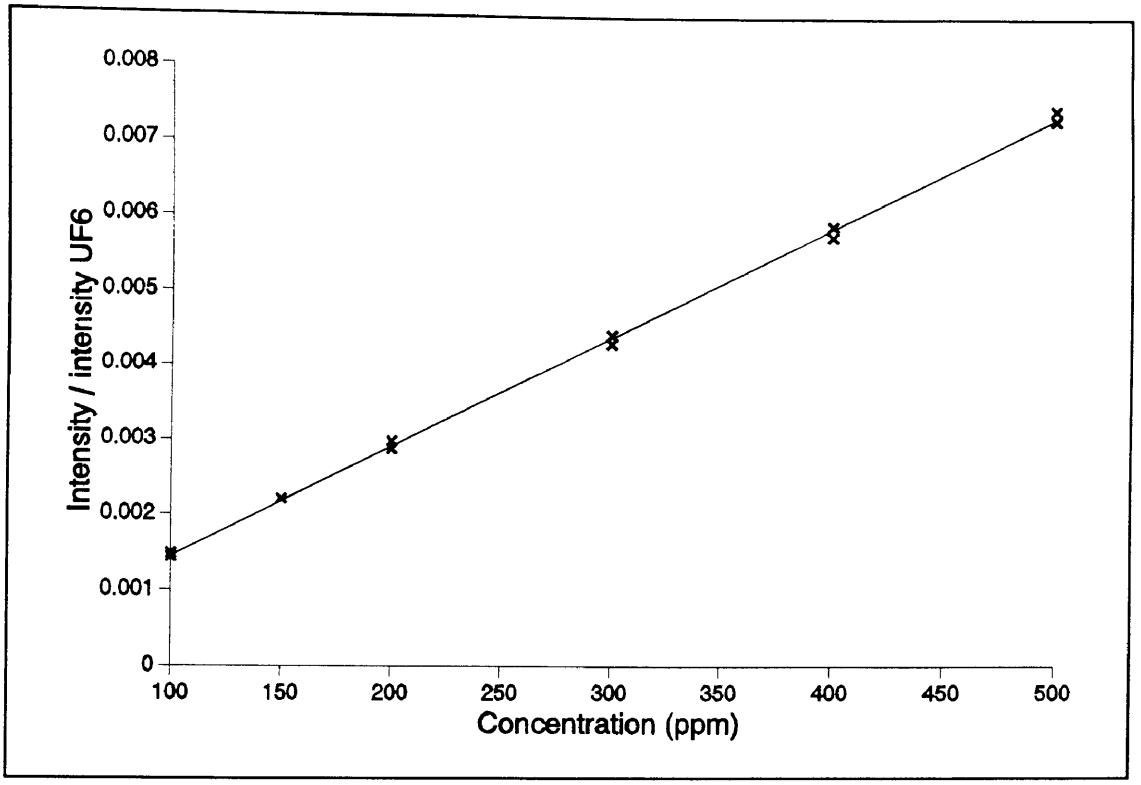


Figure 4.13 Relative response of SO_2F_2

4.5 Comparison of results achieved using internal and external calibration methods

A histogram was determined of the measured to prepared concentration for Cl_2 and Freon-11, Figures 4.14 and 4.15 respectively, to compare the results of the two approaches. The external calibration data were calculated using linear regression for each standard, and then the concentration was determined using this curve, whereas the internal standard results were calculated using the averaging method, as used by the program introduced in this thesis, to eliminate minor variations caused by inaccurate standards.

No significant differences were observed between the two methods, although both showed slight deviations from the normal distribution curve. This may be attributed to inaccuracies in the standards, which would lead to a wider distribution curve. The obvious advantages of the

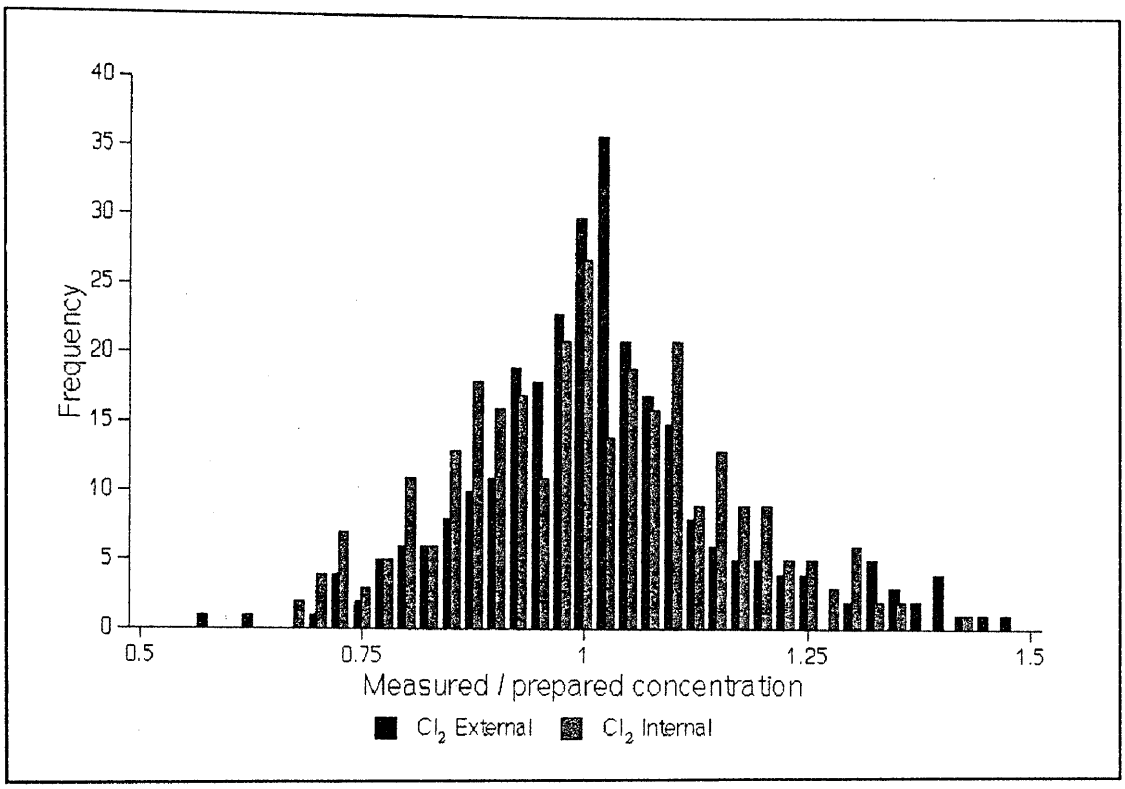


Figure 4.14 Histogram of chlorine for internal and external calibrations

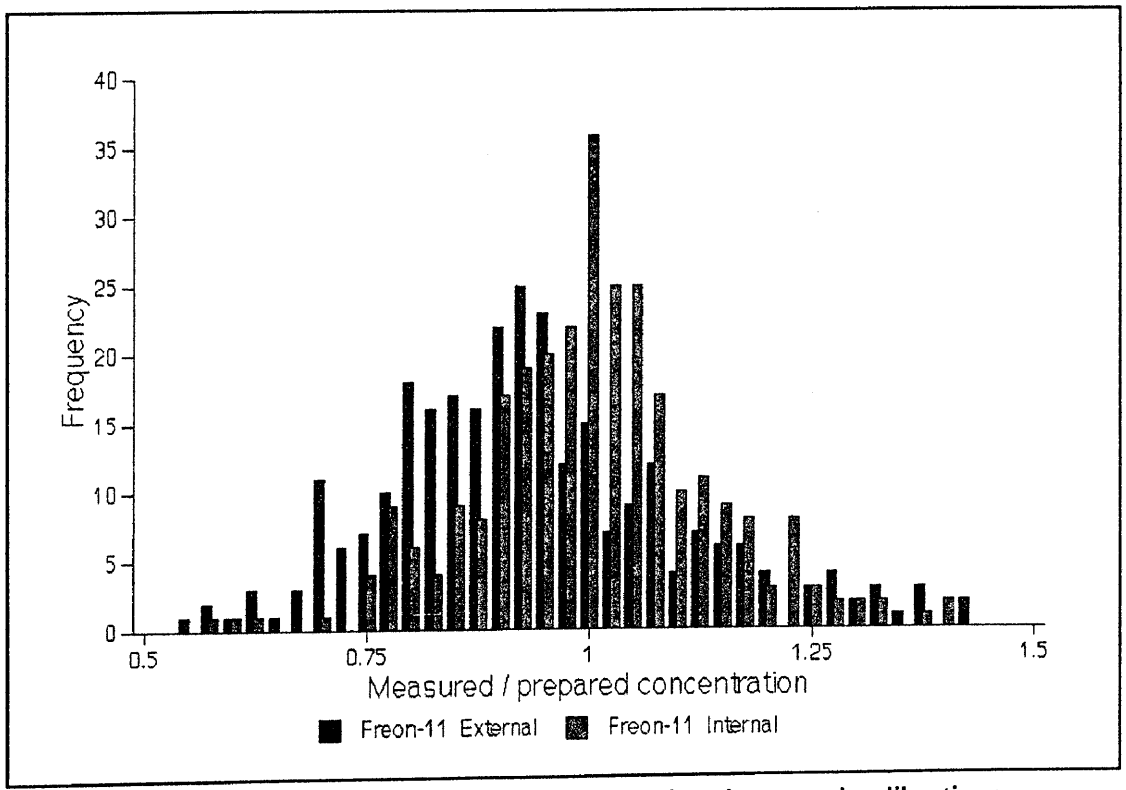


Figure 4.15 Histogram of Freon-11 for internal and external calibrations

internal standard method will become apparent in the following sections

4.6 Improvements in precision through the use of multiple internal standards

The nitrogen concentration was determined by using each of the five UF_x^{2+} fragments as internal standards, and the relative precision of the results was calculated. The concentration was then determined by using the average value of all five determinations. The results of the calculations are given in Table 4.4.

Table 4.4 N_2 concentration determined using UF_x^{2+} internal standards

U^{2+}	UF^{2+}	UF_2^{2+}	UF_3^{2+}	UF_4^{2+}	$\bar{x}$
2.18 %	2.05 %	2.26 %	2.27 %	2.34 %	2.22 %
2.20 %	2.08 %	2.27 %	2.31 %	2.38 %	2.25 %
2.24 %	2.09 %	2.24 %	2.35 %	2.44 %	2.27 %
2.22 %	2.05 %	2.31 %	2.27 %	2.36 %	2.24 %
2.22 %	2.09 %	2.32 %	2.28 %	2.37 %	2.26 %
2.22 %	2.10 %	2.31 %	2.26 %	2.36 %	2.25 %
2.21 %	2.04 %	2.33 %	2.30 %	2.39 %	2.25 %
2.22 %	2.09 %	2.32 %	2.27 %	2.36 %	2.25 %
2.21 %	2.06 %	2.30 %	2.25 %	2.34 %	2.23 %
2.22 %	2.10 %	2.30 %	2.25 %	2.34 %	2.24 %
2.20 %	2.04 %	2.31 %	2.26 %	2.36 %	2.23 %
2.28 %	2.04 %	2.22 %	2.20 %	2.23 %	2.19 %
2.14 %	2.06 %	2.32 %	2.35 %	2.48 %	2.27 %
Std 0.03 %	0.02 %	0.03 %	0.04 %	0.06 %	0.02 %
Rsd 1.4%	1.1%	1.4%	1.8%	2.4%	0.8%

The average $\bar{x}$ is a quantity calculated from the measured quantities

$x_1, x_2, \ldots, x_n$. The standard error of any function of $x_1, x_2, \ldots, x_n$, namely, $f(x_1, x_2, \ldots, x_n)$ can be determined as a linear combination of the individual standard errors using propagation of error theory[27].

$$\sigma = \sqrt{\sum_{i=1}^{n} \sigma_{x_i}^2 \left(\frac{\partial f}{\partial x_i}\right)^2}$$

The mean is defined as $\bar{x} = \dfrac{\sum_{i=1}^{n} x_i}{n}$

Since we are considering only the random error in the measurements, the x_i's may be considered independent, and their mutual correlation coefficients can be assumed to be zero.

$$\therefore \frac{\partial \bar{x}}{\partial x_i} = \frac{1}{n}$$

$$\therefore \sigma = \sqrt{\sum_{i=1}^{n} \sigma_{x_i}^2 \left(\frac{\partial \bar{x}}{\partial x_i}\right)^2}$$

$$= \sqrt{\sum_{i=1}^{n} \sigma_{x_i}^2 \left(\frac{1}{n}\right)^2}$$

$$= \sqrt{\frac{1}{n^2} \sum_{i=1}^{n} \sigma_{x_i}^2}$$

The variance for each measurement is constant

$$\therefore \sum_{i=1}^{n} \sigma_{x_i}^2 = n\, \sigma_{x_i}^2$$

$$\therefore \sigma = \sqrt{\frac{1}{n^2} n\, \sigma_{x_i}^2}$$

$$= \frac{\sigma_{x_i}}{\sqrt{n}}$$

The precision is inversely proportional to the square root of the number of observations made. Consequently, by using five internal standards the precision is improved by a factor of 2. It could be reasoned, that the same increase in precision would have been obtained by an increased number of measurements on the same internal standard peak. However, mass discrimination and peak overlap could cause a substantially incorrect measurement from a single standard. The internal standard method improves the accuracy of the determination.

4.7 Matrix effects

A number of gas mixtures were prepared, with combinations of the impurities at their normal concentration levels in the UF_6 process gas and were analysed to investigate the influence of matrix effects. From the data, which are shown in Table 4.5, it is clear that the presence of other impurities at the levels normally encountered in UF_6, does not have an influence on the quantification of a particular impurity. However, some of the samples contained abnormally high nitrogen levels. Although samples with a particularly high nitrogen content are not regularly analysed using the RRF approach, due to the non-linearity of the RRFs at high concentrations, it is important to determine the maximum nitrogen concentration that can be tolerated.

Table 4.5 Influence of matrix effects on the RRFs

Compound	$\bar{x}$	Max	Min	D_Ave	D_Max	D_Min
CF4	1.09E-4	1.14E-4	1.03E-4	1%	5%	-5%
F2	1.52E-5	1.59E-5	1.45E-5	1%	5%	-4%
N2	7.02E-9	7.35E-9	6.67E-9	0%	5%	-5%
O2	6.12E-9	6.37E-9	5.82E-9	1%	5%	-4%
PF5	2.25E-6	2.36E-6	2.15E-6	1%	6%	-3%
SF6	1.47E-5	1.50E-5	1.36E-5	4%	6%	-4%
SO2F2	1.40E-5	1.48E-5	1.38E-5	-4%	0%	-6%
Cl2	3.77E-4	4.02E-4	3.51E-4	1%	8%	-6%
Freon-11	3.47E-4	3.63E-4	3.24E-4	2%	6%	-5%

Where:

- $\bar{x}$, Max and Min are the mean, maximum and minimum RRFs respectively, measured for each compound;
- D_Ave, D_Max and D_Min are the differences between the mean, maximum and minimum from the RRFs as determined in Table 4.3.

The limits of the method were observed by plotting the $^{235}UF^{2+}$ peak vs the nitrogen peak heights (Table 4.6 and Figure 4.16). Deviation from the straight line indicates the limit of the method, and the concentration determined at this point was found to be about 25 %.

The program has an automatic alarm if the UF_6 peak heights decrease by more than 20 %. In these circumstances it uses the average UF_6 peak heights determined during the day, instead of the actual UF_6 peak heights, with the assumption that the response of the instrument for the impurity is only dependent on the partial pressure of that impurity and not on the total pressure in the ion source.

Table 4.6 Variation in RRF vs N_2 concentration

Concentration	I(N2/UF^{2+})	RRF
1%	0.00007	0.006963
2%	0.00014	0.007009
2%	0.00014	0.007023
4%	0.000282	0.007043
4%	0.000284	0.007104
5%	0.000349	0.006980
6%	0.000423	0.007055
6%	0.000416	0.006930
8%	0.000565	0.007062
8%	0.000559	0.006982
10%	0.000695	0.006948
10%	0.000709	0.007092
10%	0.000699	0.006994
12%	0.00082	0.007014
17%	0.001148	0.006949
21%	0.001527	0.007208
23%	0.001706	0.007417
30%	0.002393	0.007950
40%	0.003822	0.009507
49%	0.005469	0.011116
58%	0.007459	0.012861

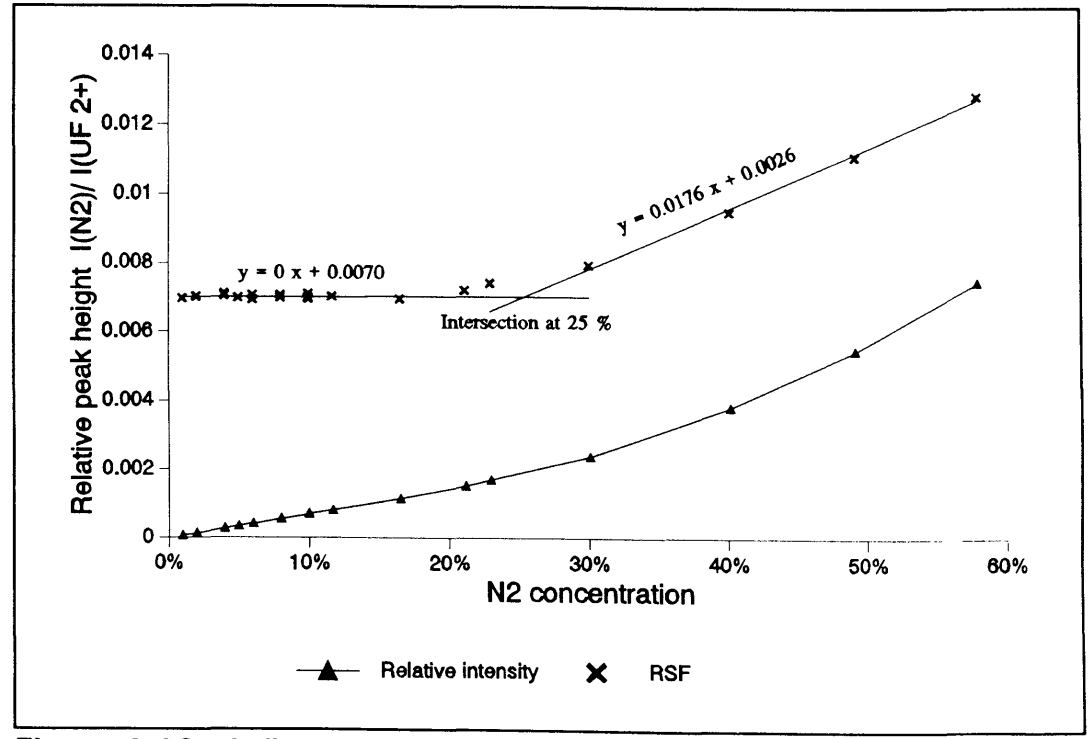


Figure 4.16 Influence of concentration

4.8 Isotopic influences

A number of samples were measured, where the isotope concentration of the UF_6 was not natural. From the theory of relative response factors, it can be seen that plotting the true concentration/measured concentration vs isotopic concentration should yield a linear graph with a slope of 1,376 (1/0,727). The data are shown graphically (Figure 4.17) and the slope was determined to be 1/0,78, which correlates with the theory. Therefore, there is no significant change in the RRFs with isotopic ratio and the concentrations can be determined using the RRF determined using natural material and adjusted for the isotopic ratio.

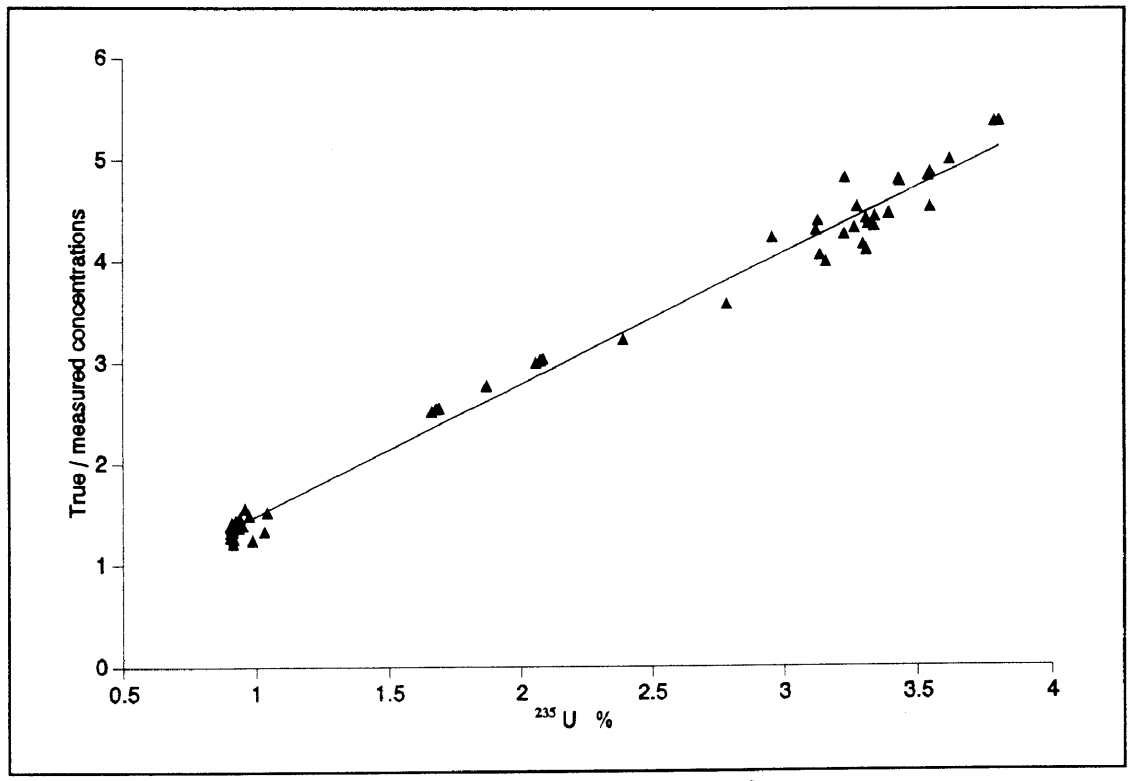


Figure 4.17 Influence of isotopic concentration

$$\frac{[i]}{UF_6} = \frac{I_i}{I_{UF_6}\, RRF_{i\ UF_6}} \quad \textit{equation 3, section 2:4}$$

$$[UF_6] = \frac{100}{x}\,[^{235}U]$$

where x is the isotopic concentration of ^{235}U, *(in percent)*

$$\therefore \frac{[i]}{UF_6} = \frac{[i]}{\frac{100}{x}\,[^{235}U]} = \frac{I_i}{I_{UF_6}\, RRF_{i\ UF_6}}$$

$$= \frac{x\,[i]}{100\,[^{235}U]}$$

This measured concentration is calculated assuming a natural isotopic composition, ie $x = 0.727$.

To correct this the measured ratio must be multiplied by $\frac{x}{0.727}$

$$i.e.\ \left(\frac{[i]}{[UF_6]}\right)_{true} = \left(\frac{[i]}{[UF_6]}\right)_{measured} \cdot \frac{x}{0.727}$$

$$\therefore \frac{\left(\frac{[i]}{[UF_6]}\right)_{true}}{\left(\frac{[i]}{[UF_6]}\right)_{measured}} = \frac{x}{0.727}$$

4.9 Detection limits

Blank concentrations were monitored to determine detection limits for each compound (Table 4.7). The IUPAC definition[28] states that: "the limit of detection, expressed as a concentration, C_L, is derived from the smallest measure, X_L, that can be detected with reasonable certainty for a given analytical procedure" . The limit of detection is, therefore, the lowest concentration level that can be determined to be statistically different from any analytical blank.

In defining C_L, IUPAC states that $X_L = X_B + k.s_B$, where:

- X_B is the average instrument signal from the blank;
- k is a numerical factor chosen in accordance with the confidence level desired. For a normal distribution, a value of k = 3 allows a confidence level of 99.86 %;
- s_B is the standard deviation of the blank measurements.

Table 4.7 Detection limits

Compound	$\bar{x}$ (blank)	s (blank)	Detection limit (ppm)
CF_4	1.3	0.6	3.0
Cl_2	0.2	0.1	0.6
Freon-11	0.2	0.1	0.7
SO_2F_2	11.0	7.0	32
SF_6	9.2	5.9	27
PF_5	16.8	14.8	61
N_2	1224	920	4000
O_2	702	1070	4000
F_2	163.7	152.8	620

CHAPTER 5
CONCLUSIONS

The method for the determination of target trace impurities in UF_6, developed for the first time in the AEC laboratories, has proved itself to be excellently suitable for routine analysis. Approximately twenty five samples are being analysed daily by this method. Both financial savings and reduced analysis time are direct results of the 90% drop in calibration requirements, when compared to the external calibration method. This was achieved without sacrificing either accuracy or precision. Furthermore, the method has been successfully utilised for automatic on-line analysis. The uniqueness of the method described in this thesis lies in the use of certain ions from the mass spectrum of the UF_6 matrix as multiple internals standards, and the use of the Gauss-Seidel iteration algorithm as the method for deconvoluting the mass spectra.

The method has now been in operation for a period of five years. During this time the need for a number of refinements have been observed, some of which have been implemented in the on-line procedure, to measure the impurities in the UF_6.

The most common occurrence is that of mass drift, where the observed masses fall outside of the 0.25 Dalton boundary, and are therefore viewed as being of a different nominal mass. Although the mass of the peak centre is displayed on the screen during the analysis, this could be missed by the analyst. The observed zero concentrations are an indication that the masses have drifted. The probability of obtaining a concentration of zero for any measurement is very slight, and this normally indicates a fault.

Experience has shown that, for this method, mass calibration at m/e 28 (N_2) and 138 ($^{238}UF_2^{2+}$) is the best approach. Although the calibration seldom drifts, it was decided that mass calibrations should be checked daily using the N_2 and $^{238}UF_x^{2+}$ peaks. This gives an early warning before the mass discrepancy is out of the allowed range.

Another factor influencing the accuracy of the results, is deterioration in peak shape. The quadrupole rods, for example, are subject to damage during cleaning by harsh abrasive materials. This causes the peak shape to degrade so that, even under the best focused conditions, a perfect peak shape cannot be obtained. An acceptable compromise must be found between peak shape and peak intensity. The analysis method first determines the peak centre, and then the signal is integrated at that mass. If the peak shape is highly fringed, this could result in a spike being mistakenly accepted as the peak centre. Consequently, the signal would be measured at the wrong mass and would be too low.

To prevent this from happening, the peak focusing method must be biased towards peak shape, without excessive loss of peak height. The final peak height should typically be around seventy percent of the maximum obtainable peak height. Best results are obtained by first focusing for maximum signal, then by adjusting focusing conditions to obtain a symmetrical peak, followed by focusing for peak shape.

The on-line procedure evaluates the peak shape daily by calculating both the resolution, according to the half-height definition, and the variance from a smoothed peak shape. These methods are not as effective as the assessment of a trained operator, therefore an improved peak evaluation method must be used and/or the peak shape should be displayed graphically, to enable the operator to evaluate the peak shape.

Peak shape normally deteriorates as a result of contamination of the quadrupole system. This must be monitored, together with abnormal changes, as a low peak height leads to a loss in response. Of particular concern, is a sudden change in peak height during the analysis. This is believed to be due to a deficiency in the energy of the electrons in the ionisation chamber, resulting in a significant reduction in the amount of sample being ionised. The problem is corrected by either increasing the electron energy through an increased cathode voltage, or by decreasing the amount of sample in the ionisation chamber by decreasing the leak rate. Both these methods increase the observed ion signals.

The program monitors the uranium signals to check for any major changes in peak intensity, which normally indicates an error. Tolerances are set at twenty percent, which is in agreement with data presented, where a twenty five percent nitrogen concentration leads to discrepancies in the RRFs. Any other problems not specifically mentioned, are normally as a direct result of the sample composition, the most common of which are due to leaking sample containers, high N_2 concentrations and unnatural isotopic uranium concentrations (which can be corrected for).

A limitation of the method is that only selected ions are monitored and other impurities may be missed or may influence the result. A solution to this would be a fast scan over the whole mass range. The contributions of the measured "target" impurities should be subtracted from this spectrum, to give an indication of the other impurities. Any significant residuals should be thoroughly investigated before the results are accepted.

The versatility of the RRF method has been shown, by applying the technique to monitor the ^{18}O concentration of di-isopropyl ether (DIPE).

As slight changes in the oxygen isotopic concentration of the DIPE lead to large changes in the isotopic concentration of the products in the enrichment process, an analytical method with very low detection limit was required. Ten percent krypton was added to the sample as an internal standard. The method was able to analyse these samples at low pressures (< 100 Pa) with a precision of better than 1 %. However, in order to achieve this, more stringent conditions were imposed on the analysis conditions, due mainly to the adsorption properties of the krypton and the source pressure influence on the observed fragmentation[29].

Total analysis time per sample for impurities in UF_6 is less than ten minutes, which means that a batch of six samples can be done within an hour. The precision of the method is within fifteen percent in the ppm concentration range. From an analytical point of view, it would be desirable, and it is probably quite feasible judging by the oxygen analyses, to reduce this to less than five percent, (the precision of the instrument). However, the limitation is the preparation of the standards of trace impurities in UF_6 which have a precision of twenty percent.

The author is unaware of any other mass spectral deconvolution method that uses the Gauss-Seidel iteration process. Other software programs tend to use matrix reduction routines. It has benefits over the matrix reduction methods of speed and simplicity of programming, as is demonstrated by the fact that the solving of equation 4 in section 3.2.1 is all that is required to deconvolute the spectrum. Coupled to the relative response factor method, which eliminates daily calibration and improves accuracy, the approach is elegantly simple.

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APPENDIX A

ANALYSIS RESULTS FORM

ATOOMENERGIEKORPORASIE VAN SA BPK

ATOMIC ENERGY CORPORATION OF SA LTD

AFDELING MASSASPEKTROMETRIE V2726

KWANTITATIEWE BEPALING VAN ONSUIWERHEDE IN UF_6

Stadium/Opstelling: BLANK
Silinder: 2477B Lot no: 2059 Oond no: F01
Afsender: N COERTSE
Datum ontleed: 1993 AUG 20
Ontleed op MS24 Rekord no: 1530

Monsterno	BLANK	MIU	01	02
Monsterdruk	8.3	8.3	5,9	10,0
Inlaatdruk	3.6	3.6	4,0	3,9
Houerno			S183	S352
Verbindings	Konsentrasie (dpm) groter as 1 %, as persent geskryf 1 % = 10 000 dpm			
CF_4	0,4	0,0	12,5	12,5
Cl_2	0,0	2,6	0,5	0,3
Freon-11	0,1	2,4	0,1	0,1
CrO_2F_2	0,0	0,0	0,0	0,1
SO_2F_2	0,0	0,1	2,9	2,2
SF_6	0,2	0,1	1,9	1,7
PF_5	29,3	8,9	728	1433
N_2	1454,4	0,0	15,7 %	18,5 %
O_2	109,1	0,0	3,7 %	4,0 %
F_2	20,8	0,0	0,57 %	0,50 %
Freon-113	0,2	0,0	1,4	1,2

Kommentaar: _____

_____

_____

Handtekening: _____

APPENDIX B

COMPUTER PROGRAM

Pascal program syntax

The following has been included to aid the reader in understanding the general structure of a pascal program. For a more detailed description of pascal syntax and programming refer to reference 30 and 31. The definitions have been copied verbatim from Turbo Pascal version 6.0's help files.

program

This is the general layout of a Turbo Pascal program:

```
program    ...  ;   { Program heading }
uses       ...  ;   { Uses clause     }
const      ...  ;   { Constants       }
type       ...  ;   { Types           }
var        ...  ;   { Variables       }
procedure  ...  ;   { Procedures      }
function   ...  ;   { Functions       }
begin
  statement;        { Statements      }
  ...
end.
```

- The program heading specifies the program's name and parameters it is purely decorative and has no meaning to the program itself. However, a variable can not have the same name as a program (or unit).
- The "uses" clause lists the units used by the program.
- The constant, variable, procedure, and function declaration parts can be listed in any order, and repeated any number of times.
- The statement part specifies the statements to be executed when the program runs.

unit

Units are the basis of modular programming in Turbo Pascal. You use units to create libraries and to divide large programs into logically related modules.

Syntax:

```
unit identifier;    { Heading }

interface           { Public symbols }
  uses ...  ;       { Uses clause }
  const ...  ;      { Constants }
  type ...  ;       { Types }
  var ...  ;        { Variables }
  procedure ...  ;  { Procedures }
  function ...  ;   { Functions }

implementation      { Private symbols }
  uses ...  ;       { Uses clause }
  label ...  ;      { Labels }
  const ...  ;      { Constants }
  type ...  ;       { Types }
  var ...  ;        { Variables }
  procedure ...  ;  { Procedures }
  function ...  ;   { Functions }

begin               { Initialization }
  statement;        { Statements }
  ...
  statement
end.
```

procedure

A procedure is a program part that performs a specific action, often based on a set of parameters.

Syntax:

```
procedure identifier;
  OR
procedure identifier ( parameters );
```

The procedure heading specifies the identifier for the procedure and the formal parameters (if any). A procedure is activated by a procedure statement.

The procedure heading is followed by

- a declaration part that declares local objects
- the statements between BEGIN and END, which specify what is to be executed when the procedure is called.

function

A "function" is a program part that computes and returns a value.
Syntax:

```
function ident : type;
  OR
function ident (parameters) : type;
```

The function heading specifies the identifier for the function, the formal parameters (if any), and the function result type. Valid result types are ordinal, real, string, and pointer types.

A function is activated by the evaluation of a function call in an expression. The function heading is followed by:

- a declaration part that declares local objects
- the statement part, which specifies the statements to be executed when the function is called.

The statement part should contain at least one statement that assigns a value to the function identifier; the result of the function is the last value assigned.

Identifiers

Identifiers denote the following:

programs	units	labels
constants	types	variables
procedures	functions	fields in records

Identifiers can be of any length, but only the first 63 characters are significant.

- The first character of an identifier must be a letter.
- The characters that follow the first one must be letters, digits,

or underscores.
Like reserved words, identifiers are not case-sensitive.

Sundry

Although identifiers are often words in the English language this does not imply that all identifiers will be correctly spelt or that all comments are linguistically correct. Often an abreviated form will be used, eg bckgrd for background. Comments are enclosed between { .. } or (* .. *)
An aid to understanding a pascal program is to read the global variables and the main BEGIN ... END. statements found at the end of the program.

The structure of the SCAN program

Units
The following units are used by the SCAN program:

- GLOBAL : All global variables are declared here.
- BZ420 : For control and communication to and from the quadrupole.
- AUXINOUT: The Turbo Pascal communication unit.
- IOLIB : A unit adapted from Turbo Pascal Toolbox, containing utility screen routines
- Unit QS is no longer used and is therefore not included.

Only the interface sections of AUXINOUT and IOLIB units are included as these units are not totally original work.

Data files
The following files are used by the program:

- RESULTS.DAT : The file of all results.
- INFO.DAT : Contains the eight peak index and RRFs.
- COEF.DAT : Coefficients of simultaneous equations matrix.
- MASS.DIR : Mass directory file
- MASS[1 ..10].DAT : List of masses to be scanned.
- PSET.DAT : Maximum concentrations permitted.
- HEADING.DAT : Client information.

```
UNIT GLOBAL; (* latest update 15/05/92 *)

INTERFACE
USES IOLIB,BZ420,CRT;
const
  MainMenu     :   Menu_Rec = (
      Num_Choices        :    6;
      Menu_Width         :    50;
      Choices            :    '012345        ';
      Descriptions       :    ('Scan the mass spectrum',
                               'Modify Parameters',
                               'Import data',
                               'Printer is',
                               'Adjust RRF"s',
                               'Exit SCAN',
                               '','','','','','','','');
      Title              :    'M A I N    M E N U';
      Prompt:' Enter choice (0-5) or use arrow keys and hit <ENTER> ');


   ModMenu     :   Menu_Rec = (
      Num_Choices        :    9;
      Menu_Width         :    50;
      Choices            :    '012345678     ';
      Descriptions       :    ('Modify masses to be scaned',
                               'Viewdata files            ',
                               'Adjust data files         ',
                               'View analysis files       ',
                               'Modify headings           ',
                               'Calculate rsf"s           ',
                               'Tabulate ALL results      ',
                               'Adjust printout table     ',
                               'Return to previous menu   ',
                               '','','','','');
      Title              :    'M O D I F Y   &   V I E W    F I L E S';
      Prompt:' Enter choice (0-8) or use arrow keys and hit <ENTER> ');

type
  Options          = record
                       State      : byte;
                       Name       : STRING79;
                       First      : Real;
                       Last       : real;
                       Values     : Array[0..12] of integer;
                     end;
```

```
Param_Rec       = record
                    Heading    : String[10];
                    name       : String[3];
                    Title      : Array[0..16] of String[10];
                  end;

InfoRec         = record
                    Element    : string[10];
                    Mass       : Array[1..7] of real;
                    RRF        : Array[1..9] of real;
                  end;

CoefRec         = record
                    element    : Array[0..20] of real;
                  end;

Printset        = record
                    table      : Array[0..20] of Boolean;
                    Limit      : Array[0..20] of real;
                  end;

UF6Type         =
     (null,me79,me86,me92,me98,me118,me127,me137,me146,me156);

Dir_rec         = record
                    Active     : Byte;
                    Filename   : Array[1..10] of String[8];
                  end;

Mass_rec        = record
                    mass       : Real ;
                    Range      : Byte ;
                  end;

Values          = Array[1..9] of real;

Results_rec     = Record
                    Stadium    : Byte;
                    Afsender   : String[20];
                    Silinderno : String[10];
                    Lotno      : String[10];
                    Oondno     : String[3];
                    Datum      : String[13];
                    Monsterno  : String[10];
                    Monsterdruk: Real;
```

```
                    Inlaatdruk : Real;
                    Houerno    : String[10];
                    Peakht     : Array[0..20] of Real;
                    Conc       : Array[0..20] of Real;
                    U235Peak   : Values;
                    Ratio      : Real;
                  end;

Hset              = Record
                    Title : Array[1..10] of String79;
                  end;

String15 = String[15];

Var

  y,z,Maxz,diractive,NoAve      : Byte;
  Dirname                       : Array[1..10] of String[8];
  mycom, mycom1                 : STRING5;
  Found                         : Boolean;
  newname                       : String[8];
  Massstr                       : String[6];
  Activestr                     : String[2];

  Infofile                      : File of InfoRec;
  Coeffile                      : File of CoefRec;
  Options_file                  : File of Options;
  Param_file                    : File of Param_Rec;
  Dir_file                      : File of Dir_rec;
  Mass_file                     : File of Mass_rec;
  Results_file                  : File of Results_rec;
  Printfile                     : File of Printset;
  Headingfile                   : File of Hset;

  Info                          : InfoRec;
  Coef                          : CoefRec;
  Chan                          : Options;
  Param                         : Param_Rec;
  Directory                     : Dir_rec;
  Masses                        : Mass_rec;
  Results                       : Results_rec;
  Report                        : Array[1..4] of Results_rec;
  Print                         : Printset;
  Heading                       : Hset;
```

```
  i,j,Loop,NoOfSamples,Sample,row,Parameter : Byte;
  x                                         : integer;
  compound                                  : String79;
  UF6                                       : UF6Type;
  UF6Name                                   : Array[UF6Type] of Real;
  Blank,BlankDone,Mixture                   : Boolean;
  Response,ModResp                          : Char;
  Ram1,Ram2                                 : ResultBuffer;
  Status                                    : ScanStsSet;
  Peak,Pcount,PcountTotal                   : Integer;
  Uratio,Upeak,UAve                         : Values;
  Mass,Intensity                            : Real;
  Int,BInt                                  : Array[0..800] of Real;

Procedure set_Options;
Procedure default;
Procedure Ttest(Rval: Values;var  Mean: Real);
Procedure Setheading;
Procedure SetUF6;
Procedure Setprint;

IMPLEMENTATION
(*********************************************************)

Procedure Ttest(Rval: Values;var  Mean: Real);
(*  This procedure calculates the mean, sigma and t for the t test    *)
(*  from this it determines the range and rejects outliers            *)
Var Tval, Sigma, sx, sx2 : real;
    i,j,Noofresults,x:Byte;
Begin
  Noofresults:= 9;
  For i:= 1 to Noofresults do If Rval[i] = 0 then
    Repeat
      for j:= i to Noofresults do Rval[j]:= Rval[j+1];
      Noofresults:= Noofresults-1;
    until Rval[i] <> 0;
  sx:= 0; sx2:=0;
  If Noofresults < 2 then Mean:= Rval[1] else
    begin
      For j:= 1 to Noofresults do
        begin
          sx := sx  + Rval[j];
          sx2:= sx2 + Rval[j]*Rval[j];
        end;
      Mean:= sx/ Noofresults;
```

```
      sigma:= SQRT( (sx2 - (sx*sx/Noofresults)) / (Noofresults-1) );
      x:= Noofresults-1;
      Tval:= exp( 0.709/x/x +1.212/x+0.673)/sqrt(x+1)* sigma;
      j:= 1;Repeat
              if (Rval[j] < Mean-Tval) or (Rval[j] > Mean+Tval)
                then begin
                  Noofresults:= Noofresults-1;
                  For i:= j to Noofresults do Rval[i]:=Rval[i+1];
                end else j:= j+1;
            until j > Noofresults;
      Mean:=0;
      For j:= 1 to Noofresults do Mean:=Mean + Rval[j];
      Mean:=Mean/Noofresults;
    end;
  end;


Procedure Setheading;
var counter:byte;
Begin
  For counter:=1 to 10 do Get_String(Heading.Title[counter],
                                     counter+10,10,1,20);
  Seek(Headingfile,0);Write(Headingfile,Heading);
end;

Procedure SetUF6;                        (*************** Set UF6 peaks
***)
  begin
    UF6Name[me79] := 78.3;
    UF6Name[me86] := 84.7;
    UF6Name[me92] := 91;
    UF6Name[me98] := 97.3;
    UF6Name[me118]:=117.5;
    UF6Name[me127]:=127;
    UF6Name[me137]:=136.5;
    UF6Name[me146]:=146;
    UF6Name[me156]:=155.5;
  end;

Procedure Setprint;
var ans:char;
Begin
  For j:=0 to 20 do Print.Table[j]:= false;
  Assign(Infofile,'INFO.DAT');Reset(Infofile);j:= 0;
  While not EOF(Infofile) do
```

```
  begin
    Seek(Infofile,j);Read(Infofile,Info);
    Write(Info.element:10,' (Y/N) ');
    ans:= readkey;
    Write(ans,' Limit (ppm) ');
    If ans in ['Y','y']
    then begin Print.Table[j]:= true;
      Readln(Print.Limit[j]);
    end else begin Print.Limit[j]:=1;writeln; end;
    j:= j+1;
  end;
  Close(Infofile);
  Assign(Printfile,'PSET.DAT');Rewrite(Printfile);Write(Printfile,Print);
  Close(Printfile);
end;

BEGIN
END.
```

```
unit BZ420; (*latest update 14/08/90    Peak_f then MID, autoranging *)

interface
uses  Crt, Dos, AuxInOut ,Turbo3, Printer ;

type  ResultRec     =    record
                           Mass          :   Real;
                           Int           :   Real;
                         end;
      ResultBuffer  =    Array[0..250] of ResultRec;
      ScanSts       =    (Empty,OverRange,CommsError,CalcError);
      ScanStsSet    =    Set of ScanSts;

      string4       =    String[4];

Var Range: Shortint;
    Height, Newheight, Delta, Newdelta, Meval, Newmass :Real;
    Region, Newregion: Char;
    Semvoltage       : Integer;

procedure Scann(First:real;Speed,Detector:byte;
               var ScanBuffer:ResultBuffer;var ScanSts:ScanStsSet;
               var Pcounted:Integer);
procedure ReportScanStatus(ScanSts:ScanStsSet);
Procedure OpenCom;
procedure GotoLocal;
Procedure Get_Sem_voltage;

implementation
type  GetSBuff      =    string[80];
      StringArray   =    Array[1..10] of String[7];

const Threshold     =    1;     (* 4=100mV   5=300mV   6=1V *)
      COM1          =    0;

var   Aux           :    Text;

procedure ClearAuxIn;
  var    Dummy          :    char;
  begin
    While AuxInReady(COM1) do Dummy:=AuxInChar(COM1);
  end;

procedure GetS(var InString: GetSBuff);
  const    LF        =   #10;
```

```
            CR          =    #13;
            Max         =    8000;
  var       i           :    integer;
            Timeout     :    integer;

  begin
    TimeOut:=0; i:=0;
    While ((not AuxInReady(COM1)) and (Timeout<Max)) do
Timeout:=succ(TimeOut);
    If TimeOut<Max then
      begin
        repeat
          i:=succ(i);
          InString[i]:=AuxInChar(COM1);
        until (InString[i] = LF) or (i=79);
        i:=i-2;
        If i<0 then i:=0;
      end;
    Instring[0]:=chr(i);
  end;

procedure DisasString(InString:GetSBuff;var Segment:StringArray;
                      var NoOfSeg:Integer);
  var    J,I      :    Integer;
  begin
    J:=0;
    Repeat
      J:=succ(J);
      I:=pos(',',InString);
      If i<>0 then
        begin
          Segment[j]:=copy(Instring,1,I-1);
          InString:=copy(InString,I+1,Length(InString)-I);
        end else Segment[j]:=Instring;
    Until ((I=0) or (J>10));
    NoOfSeg:=J;
  end;

Procedure Get_Sem_Voltage;
var instring :  GetSBuff;
    code, NoOfParts             :  Integer;
    Part                        :  StringArray;
Begin
  Writeln(Aux,'RDE');   (* Get SEM VOLTAGE *)
  GetS(InString);
```

```
  DisasString(Instring,Part,NoOfParts);
  Semvoltage:= 1;
  Val(Part[5],SemVoltage,Code);
  If SemVoltage<=1 then
    begin Write(' Enter the sem voltage ');Readln(Semvoltage);end;
 end;

procedure GotoLocal;
  begin  Writeln(Aux,'CTR0'); end;

function QMGOK:boolean;
  var   Dummy           :    char;
        StatusWord      :    GetSBuff;
  begin
    QMGOK:=false;
    ClearAuxIn;
    Writeln(Aux,'ERW');
    GetS(StatusWord);
    If Length(StatusWord)=16 then QMGOK:=true;
  end;

procedure WaitForScanCompletion;
  const  Max            =   1000;
  var    StatusWord     :   GetSBuff;
         JobDone        :   Char;
         TimeOut        :   Integer;
  begin
    TimeOut:=0;
    JobDone:='0';
    repeat
      Delay(500);
      ClearAuxIn;
      Writeln(Aux,'STW');
      GetS(StatusWord);
      If length(StatusWord)=16 then JobDone:=StatusWord[7];
      TimeOut:=succ(TimeOut);
    until (JobDone='1') or (TimeOut>Max);
  end;

Function QMGBufferEmpty:Boolean;
  var Bit4          :   Char;
      ErrorWord     :   GetSBuff;
  begin     Delay(50);     ClearAuxIn;
    Writeln(Aux,'STW');
    GetS(ErrorWord);
```

```
    Bit4:=ErrorWord[5];
    If Bit4='1' then QMGBufferEmpty:=true else QMGBufferEmpty:=false;
  end;

procedure Scann; (* See Interface section for parameter list *)
  const     ENQ                    =   #05;

  Procedure InitializeScan;
  Begin                            { HALT,MONO,CHANNEL0,STATE,-->SPEED }
    Writeln(Aux,'HAL,OPM0,CHA0,STA1,FIL0');
    Writeln(Aux,'DET',Detector);
    If Detector= 1 then Writeln(Aux,'SEM',Semvoltage)
                   else Writeln(Aux,'SEM1');
    Writeln(Aux,'THR',Threshold);
    Writeln(Aux,'WID2');
  end;

  Procedure DoScan(mode:String4;scanspeed:byte;Firstmass:real);
  var  ScanType,ChannelNo,PCount,i :  Integer;
       IntensityIn,MassIn,IntHigh  :  Real;
       code, NoOfParts             :  Integer;
       InString                    :  GetSBuff;
       Part                        :  StringArray;
       Rangeok                     :  Boolean;
  Begin
    Writeln(Aux,mode);
    Writeln(Aux,'SPE',ScanSpeed);
    Writeln(Aux,'FIR',Firstmass:6:2);
    rangeok := false;

    repeat
      If Range > 7 then begin Range:= 7; Rangeok:= true;end;
      Writeln(Aux,'RAN',Range);
      Delay(500);
      Writeln(Aux,'CYC1,RUN,STO');
      WaitForScanCompletion;
      Pcount:=1; (*** ensure at least one execution of loop ***)
      If not QMGBufferEmpty then
      begin
        Writeln(Aux,'HEA');
        GetS(InString);
        DisasString(Instring,Part,NoOfParts);
        If NoOfParts=3 then
        begin
          Val(Part[1],ScanType,Code);
```

```
          Val(Part[2],ChannelNo,Code);
          Val(Part[3],PCount,Code);
        end  else ScanType:=99; (* Error in header data *)

        If ScanType > 9 then Pcount:=0;
        IntHigh:= 0;Height:=0;
        If Pcount <> 0 then for i:= 1 to Pcount do
        begin
          Delay(20);
          Writeln(Aux,ENQ);
          GetS(InString);
          DisasString(Instring,Part,NoOfParts);
          Val(Part[1],IntensityIn,code);
          If ScanType = 2 then Val(Part[2],MassIn,Code)
            else MassIn:= Firstmass;
          If IntensityIn > IntHigh then If Abs(MassIn-First) < 0.30
            then begin IntHigh:=IntensityIn; Meval:=MassIn; end;
        end; {Pcount<>0}
        Height:= IntensityIn*exp(-Range*Ln(10))/100000;

        If ScanType = 2 then Rangeok:= true { Don't autorange for Peak_F}
          else If IntHigh > 1 then Range:= Range - 2
            else If IntHigh < 0.01 then Range:= Range + 1
              else Rangeok:= true;
        If Range > 7 then begin Range:= 7; Rangeok:= true;end;
      end else Range:= Range + 2;{QMGBuffer empty}

    until Rangeok ;
  end;

begin
  ScanSts:=[];
  If QMGOK then
  begin
    InitializeScan;
    GotoXY(10,11); Write('Scanning for m/e: ',First:6:2);
    DoScan('CHM2',7 ,First);        { Fast Scan to find range }
    Meval:= First;
    DoScan('CHM4',10,First-1);      { Find peak max           }
    DoScan('CHM2',11,Meval);        { Measure at max          }

    Inc(PCounted);
    ScanBuffer[PCounted].Mass:= Meval;
    ScanBuffer[PCounted].Int:= Height;
    GotoXY(10,22); Write('m/e: ',First:6:2,' found at ',Meval:6:2,
```

```
                                Intensity: ',Height:10);

  end else ScanSts:= ScanSts + [CommsError];
  If PCounted=0 then ScanSts:=ScanSts+[Empty];
end;

procedure ReportScanStatus(ScanSts:ScanStsSet);
  var           I                 :  Integer;
  begin
    Writeln;
    Write('Scan status: ');
    If Empty in ScanSts then Write('No data available, ');
    If Overrange in ScanSts then Write('Some data overrange, ');
    If CommsError in ScanSts then Write('Communication error, ');
    If CalcError in ScanSts then Write('Calculation error, ');
    If ScanSts=[] then write('No severe errors detected');
    Writeln;
  end;

(* Initialization code for this unit *)
Procedure OpenCom;
begin
    AssignAux(Aux,0,$E3);
    Rewrite(Aux);
    ClearAuxIn;
    Writeln(Aux,'CTR1');  (* QMG420 remote enable, console disable *)
    Writeln(Aux,'HAL');   (* Force HALt *)
end;
end.



unit AUXINOUT;
{       Copyright (c) 1985, 87 by Borland International, Inc.            }

interface

uses Dos;

procedure AssignAux(var F: Text; Port,Params: Word);
procedure AuxInit(Port,Params: Word);
function  AuxInChar(Port: Word): Char;
procedure AuxOutChar(Port: Word; Ch: Char);
function  AuxInReady(Port: Word): Boolean;
```

```
UNIT IOLIB;

INTERFACE

USES TURBO3,CRT,DOS,PRINTER;

type    STRING79        =          string[79];
        STRING10         =          string[10];
        STRING5         =          string[5];
        RESPONSE_TYPE   =          (NO_RESPONSE,ARROW,KEY,RETURN);
        MOVEMENT        =          (NONE,LEFT,RIGHT,UP,DOWN);

        Menu_Rec        = Record
                            Num_Choices    :   Integer;
                            Menu_Width     :   Integer;
                            Choices        :   Array[1..14] of Char;
                            Descriptions   :   Array[1..14] of String79;
                            Title          :   String79;
                            Prompt         :   String79;
                          end;

        Toggle_Rec      = Record
                            Num_Choices    :   Integer;
                            Strings        :   Array[0..8] of String79;
                            Locations      :   Array[0..8] of Integer;
                          end;

Const
     Print_Toggle:    Toggle_Rec = (
       Num_Choices:   4;
       Strings:       ('a','b','c','d','','','','','');
       Locations:     (5,20,35,43,50,0,0,0,0));

CONST    CR              =   #13;
         LF              =   #10;

Var          prt          :Boolean;
             k            :integer;
             year,month,day,dayofweek:word;
             datum        :STRING10;
             monthname    : array[1..12] of string[5];

Procedure setmonths;
Procedure Get_date(var new:STRING10);
Procedure Clear_window(no:Byte);
```

```
Procedure Print_Window(no:Byte;sentence:STRING79;row,col,high:Byte);
Procedure Get_Char(var out:STRING5);
Procedure Set_Video (ATTRIBUTE: integer);
Procedure Set_Video_Myne (ATTRIBUTE: integer);
Procedure SetVideoHerc(ATTRIBUTE:integer);
Procedure Put_String (OUT_STRING: STRING79;
                      LINE, COL, ATTRIB: integer);
Procedure Put_Centered_String(Out_String:String79;
                              Line,Attrib:Integer);
Procedure Put_Prompt (OUT_STRING: STRING79;LINE, COL: integer);
Procedure GET_STRING (var IN_STRING: STRING79;
                            LINE, COL,ATTRIB, STR_LENGTH: integer);
Procedure  Get_Real  (var  NUMBER:  real;
                          LINE, COL, ATTRIB,NUM_LENGTH,  NUMDEC:  integer);
Procedure Get_Integer  (var NUMBER:  integer;
                             LINE, COL,ATTRIB, NUM_LENGTH:  integer);
Procedure Get_Response( var RESPONSE    : RESPONSE_TYPE;
                        var DIRECTION   : MOVEMENT;
                        var KEY_RESPONSE: char);
Procedure  Get_prompted_String  (var IN_STRING:  STRING79;
                               INATTR,STR_LENGTH:  integer;
                                         STRDESC:  STRING79;
                               DESCLINE, DESCCOL:  integer;
                                          PROMPT:  STRING79;
                                    PRLINE,PRCOL:  integer);
Procedure  Get_Prompted_Real  (var INNUMBER:    real;
                   INATTR, NUM_LENGTH, INNUMDEC:    integer;
                                       STRDESC:    STRING79;
                          DESCLINE, DESCCOL:    integer;
                                        PROMPT:    STRING79;
                                   PRLINE,PRCOL:    integer);
Procedure  Get_Prompted_Integer (var INNUMBER:     integer;
                             INATTR, NUM_LENGTH:     integer;
                                         STRDESC:     STRING79;
                             DESCLINE, DESCCOL:     integer;
                                          PROMPT:     STRING79;
                                    PRLINE,PRCOL:     integer);
Procedure Bell;
Procedure PrintScreen;
Procedure Pause;
Procedure Display_Frame(Num_Lines,Num_Cols: Integer);
Procedure Display_Menu(Menu: Menu_Rec);
Procedure Get_Menu_Response(Menu:Menu_Rec;
                            var Users_Choice: Char);
procedure put_1Line_Toggle (Toggle:Toggle_rec;line,choice:integer);
```

```
procedure Get_lLine_Toggle (     Toggle: Toggle_REC;
                                  LINE : integer;
                             var CHOICE: integer;
                                 PROMPT: STRING79;
                           PRLINE, PRCOL: integer);

procedure put_lcol_Toggle (toggle:toggle_rec;col,choice:integer);
procedure Get_lcol_Toggle (      Toggle: Toggle_REC;
                                   COL : integer;
                             var CHOICE: integer;
                                 PROMPT: STRING79;
                           PRLINE, PRCOL: integer);
```

```
Procedure Print_Window(no:Byte;sentence:STRING79;row,col,high:Byte);
Procedure Get_Char(var out:STRING5);
Procedure Set_Video (ATTRIBUTE: integer);
Procedure Set_Video_Myne (ATTRIBUTE: integer);
Procedure SetVideoHerc(ATTRIBUTE:integer);
Procedure Put_String (OUT_STRING: STRING79;
                      LINE, COL, ATTRIB: integer);
Procedure Put_Centered_String(Out_String:String79;
                              Line,Attrib:Integer);
Procedure Put_Prompt (OUT_STRING: STRING79;LINE, COL: integer);
Procedure GET_STRING (var IN_STRING: STRING79;
                            LINE, COL,ATTRIB, STR_LENGTH: integer);
Procedure  Get_Real  (var  NUMBER:  real;
                          LINE, COL, ATTRIB,NUM_LENGTH,  NUMDEC:  integer);
Procedure Get_Integer  (var NUMBER:  integer;
                             LINE, COL,ATTRIB, NUM_LENGTH:  integer);
Procedure Get_Response( var RESPONSE    : RESPONSE_TYPE;
                        var DIRECTION   : MOVEMENT;
                        var KEY_RESPONSE: char);
Procedure  Get_prompted_String  (var IN_STRING:  STRING79;
                               INATTR,STR_LENGTH:  integer;
                                         STRDESC:  STRING79;
                               DESCLINE, DESCCOL:  integer;
                                          PROMPT:  STRING79;
                                    PRLINE,PRCOL:  integer);
Procedure  Get_Prompted_Real  (var INNUMBER:    real;
                   INATTR, NUM_LENGTH, INNUMDEC:    integer;
                                       STRDESC:    STRING79;
                          DESCLINE, DESCCOL:    integer;
                                        PROMPT:    STRING79;
                                   PRLINE,PRCOL:    integer);
Procedure  Get_Prompted_Integer (var INNUMBER:     integer;
                             INATTR, NUM_LENGTH:     integer;
                                         STRDESC:     STRING79;
                             DESCLINE, DESCCOL:     integer;
                                          PROMPT:     STRING79;
                                    PRLINE,PRCOL:     integer);
Procedure Bell;
Procedure PrintScreen;
Procedure Pause;
Procedure Display_Frame(Num_Lines,Num_Cols: Integer);
Procedure Display_Menu(Menu: Menu_Rec);
Procedure Get_Menu_Response(Menu:Menu_Rec;
                            var Users_Choice: Char);
procedure put_1Line_Toggle (Toggle:Toggle_rec;line,choice:integer);
```

```
    Writeln(Pfile,' ‖');
  end;

Procedure writeconc;
begin
  Assign(Printfile,'PSET.DAT');Reset(Printfile);Read(Printfile,Print);
  Assign(Infofile,'INFO.DAT');Reset(Infofile);j:= 0;
  While not EOF(Infofile) do
  begin
    Seek(Infofile,j);Read(Infofile,Info);
    If Print.Table[j]=true then
    Begin
      Write(Pfile,' ‖   ',Info.element:10,' ' );
      for i:= 1 to NoofSamples do
        begin If Report[i].Conc[j] > 1E6 then Report[i].Conc[j]:= 1E6;
          Write(Pfile,' | ');
          If Report[i].Conc[j] > Print.Limit[j]
          then begin
            Write(Pfile,'>');
            Report[i].Conc[j] := Print.Limit[j];
          end else Write(Pfile,' ');
          If Report[i].Conc[j] < 10000 then
            Write(Pfile,Report[i].Conc[j]:6:1,'  ') else
            Write(Pfile,Report[i].Conc[j]/10000:6:1,' %');
        end;
      for i:= NoofSamples+1 to 4 do Write(Pfile,' |          ');
      Writeln(Pfile,' ‖');
    end;
    j:= j+1;
  end;
  Close(Infofile);Close(Printfile);
end;

Procedure PrintReport;
begin
  clrscr;
  If (not waiting) and ((NoOfSamples = 1) or (NoOfSamples = 3))
    then writeln(Pfile,#12);  {Formfeed}
  { set printer, unidirectional, NLQ, Sanserif, empasised }
  write(Pfile,#27,#85,1);  write(Pfile,#27,#120,1);
  write(Pfile,#27,#107,1); writeln(Pfile,#27,#69);
  Print_title;
  Print_heading;
  writestr('Monsterno');
  writeval('Monsterdruk');
```

```
  writeval('Inlaatdruk');
  writestr('Houerno');
  Print_subheading;
  writeconc;
  Print_footnote;
  WriteLn(Pfile,#12);  {printer form feed}
  write(Pfile,#27,#64);{reset printer}
end;

Procedure Sendit( code:byte);
begin
  If code=0 then Assign(pfile,'PRN') else Assign(pfile,'LST1.TXT');
  If code=0 then waiting := false else waiting:= true;
  Rewrite(Pfile);  PrintReport;  close(Pfile);
end;

Procedure Printit;
Var string80 : string[82];
begin
  If waiting then
  begin
    Assign(pfile,'LST1.TXT');  Reset(Pfile);
    while not EOF(Pfile) do
    begin    Readln(Pfile,string80);    Writeln(LST,string80);  end;
    close(Pfile);
  end;
  waiting:= false;
end;

Procedure QUADSTR;
  Begin
    ClrScr;
    Display_Frame(3,50);
    Put_Centered_String('QUADSTAR ASCII FILE PROCESSING',12,2);
    ReadDataFileIntoArrays(UserSelectedFile);
    Start:=1;
    Fin:=2;
    IntegrateCycles;
  end;

Function ME2(me:real):integer;
  begin  ME2:=Trunc(2*(me+0.25));  end;

Procedure Includepeak;
Var Newmass                :integer;
```

```
begin
   Newmass:= ME2(Mass);
   Int[Newmass]:=Int[Newmass]+Intensity;
   For UF6:= me79 to me156 do
     begin
       If UF6Name[UF6]*2 = Newmass
         then UPeak[ord(UF6)]:=Int[Newmass]+BInt[Newmass];
       If (Newmass-2 = UF6Name[UF6]*2) or (Newmass-3 = UF6Name[UF6]*2)
         then If UPeak[ord(UF6)] = 0 then URatio[ord(UF6)]:= 0
         else URatio[ord(UF6)]:= UPeak[ord(UF6)] /
              ( UPeak[ord(UF6)]+Int[Newmass]+BInt[Newmass]);
     end;
end;

Procedure Showheading;
begin
  Clrscr;
  With Results do
  begin
    Writeln(' ',Datum:13,' ':18,'MS ',MSNO,' ':20
           ,'Record no:',Filesize(Results_file));
    Writeln(' Stadium/Opstelling: ',Heading.Title[Stadium]:20
           ,'  Afsender: ',Afsender:20);
    Writeln(' Silinder : ',Silinderno:10,'      Lot no: '
           ,Lotno:10,'    Oond no: ',Oondno:3);
    Writeln(' Monsterno: ',Monsterno:10,'     Houerno: ',Houerno:10);
    Writeln(' Monsterdruk: ',Monsterdruk:6:1
     ,'       Inlaatdruk: ',Inlaatdruk:6:1);
  end;
end;

Procedure Skipmeasurement;
var i: Byte;
begin
  with results do
  begin
    for i:= 0 to 20 do begin Peakht[i]:= 0; Conc[i]:= 0; end;
    for i:= 1 to 9  do U235Peak[i]:= 0;
    Ratio := 0; Inlaatdruk:= 0;
  end;
  clrscr;
end;

Procedure Calculations;          (*** Calculate peak heights and conc *)
Var
```

```
  Peaks,Itteration                : Byte;
  Peakconc                        : Values;
  Cal                             : Array[0..20] of Real;
  Lowval                          : Real;

Begin                             (*************   Initialize values ***)
  assign(Infofile,'INFO.dat'); reset(Infofile);
  assign(Coeffile,'Coef.dat'); reset(Coeffile);
  If Blank then For x:= 0 to 800 do   BInt[x]:= 0;
  If Blank then For x:= 0 to 20 do Cal[x]:= 0;
  For x:= 0 to 800 do   Int[x]:= -BInt[x];
  For i:= 1 to 9   do  begin UPeak[i]:= 0; Uratio[i]:= 0; end;
  For i:= 0 to 20  do Results.Peakht[i]:= 0;

  If Response = '0'                                (***  use scan data ****)
  then  begin  For Peak:=1 to PcountTotal do
          begin
            Mass :=  Ram1[Peak].Mass ; Intensity:= Ram1[Peak].Int ;
            Includepeak;
          end; end
  else  begin                    (* import data manually or from quadstar *)
  Write(' Read data from quadstar or type values in (Q/M)');
  Readln(Response);
  If upcase(Response)='Q'
    then begin
           QUADSTR;
           For i:=1 to NoOfChannels do
             begin
               Mass:= MassRange[i].MassNo;
               If trunc(Mass) in [117,118] then Mass:=117.5;
               If trunc(Mass) in [136,137] then Mass:=136.5;
               If trunc(Mass) in [155,156] then Mass:=155.5;
               Intensity:= ItotAve[i];
               Includepeak;
             end;
         end
    else begin
           Write('Enter the number of peaks ');Readln(Peaks);
           For Peak:=1 to Peaks do
           begin
             Writeln('Enter the mass and the intensity ');
             Readln(Mass);ReadLn(Intensity);
             Includepeak;
           end;
        end;
```

```
      end;
   Clrscr;
   Textcolor(31);Writeln('  Pomp monster weg asseblief ');Textcolor(15);
   Showheading;
  If Blank then For x:= 0 to 800 do   BInt[x]:=Int[x];
  If (Blank) and (NoAve=0) then
  begin
    NoAve:= 1;
    For UF6:= me79 to me156 do UAve[ord(UF6)]:= UPeak[ord(UF6)];
  end;
  For UF6:= me118 to me156 do Results.U235Peak[ord(UF6)]:=
UPeak[ord(UF6)];
                                (**********   Checking UF6 Peaks   ***)
   If  ( UPeak[5] > 0.7*UAve[5]/NoAve) and
       ( UPeak[5] < 1.3*UAve[5]/NoAve) and
       ( UPeak[6] > 0.7*UAve[6]/NoAve) and
       ( UPeak[6] < 1.3*UAve[6]/NoAve) then begin
     Write('         UF6 SPECTRUM ok                 ');
      NoAve:= NoAve + 1;
      For UF6:= me79 to me156 do
      UAve[ord(UF6)]:= UAve[ord(UF6)] + UPeak[ord(UF6)];
    end else begin
      Write('        WARNING: ERROR IN UF6 SPECTRUM  ');
      For UF6:= me79 to me156 do UPeak[ord(UF6)]:= UAve[ord(UF6)]/NoAve;
    end;
  If Blank then Writeln(' BLANK') else writeln;
  For Itteration:=1 to 3 do       (******************* Do Itteration ***)
    begin
      i:=0; Seek(Infofile,0);
      While not EOF(Infofile) do
        begin
          Seek(Infofile,i); Read(Infofile,Info);
          Seek(Coeffile,ME2(Info.Mass[2]) ); Read(Coeffile,Coef);
          if Coef.element[i] = 0 then Lowval:= 0 else
          Lowval:=Int[ME2(Info.Mass[2])]/Coef.element[i];
          Seek(Coeffile,ME2(Info.Mass[1]) ); Read(Coeffile,Coef);
          If Coef.element[i] <> 0 then
            begin
              Results.Peakht[i]:= Int[ME2(Info.Mass[1])];
              For j:= 0 to 20 do
                If (j <> i)  and (Coef.element[j] <> 0)
                then Results.Peakht[i]:= Results.Peakht[i]
                  - Coef.element[j] * Results.Peakht[j];
              Results.Peakht[i]:= Results.Peakht[i]/Coef.element[i];
              If Results.Peakht[i] > Lowval
```

```
                then Results.Peakht[i]:= Lowval;
              If Results.Peakht[i] < 0      then Results.Peakht[i]:= 0;
            end;i:=i+1;
        end;
    end;


                                (***************** Writing Results ***)
Seek(Infofile,0);
Textbackground( 9);Write('  compound,');
Textbackground(12);Write(' Peak height,');
Textbackground(13);Writeln(' Conc (ppm) ');
Textbackground( 0);Writeln;i:=0;
While not EOF(Infofile) do
  begin
    Seek(Infofile,i);Read(Infofile,Info);
    Seek(Coeffile,ME2(Info.Mass[1]) );Read(Coeffile,Coef);
    Textbackground( 9);Write(Info.Element :10,' ');
    Textbackground(12);Write(Results.Peakht[i]:9     ,' ');
    Textbackground( 0);Write('   ');
    Textbackground(13);
                                          (*** Calc conc using rsfs **)
    If Results.Peakht[i] = 0 then Results.Conc[i]:= 0 else
      begin                               (*** Do t test on results **)
        For UF6:= me79 to me156 do
          If  UPeak[ord(UF6)] <> 0  then
            Peakconc[ord(UF6)]:=
              Results.Peakht[i]*Info.RRF[ord(UF6)]/UPeak[ord(UF6)]
            else Peakconc[ord(uf6)]:= 0;
        Ttest(Peakconc,Results.Conc[i]);
      end;

    If ( Cal[i] = 0 ) and ( Results.Peakht[i] <> 0) and ( not Blank )
      then Cal[i]:= Results.Conc[i]/Results.Peakht[i];
    write(Results.Conc[i]:10:2);

    i:=i+1;If i mod 2 = 0 then writeln else write('      ');
  end;
    Writeln;
    Ttest(URatio,Results.Ratio);
    If Results.Ratio > 1 then Results.ratio := 1;
    If Results.Ratio < 0.00001 then Results.ratio:= 0;
    writeln(' 235/238 ratio is ' ,Results.Ratio*100:6:3,' %');
close(Infofile); Close(Coeffile);
Pause; Textbackground(0)
```