



Relative Sensitivity

RS Measurements of Gases

Introduction

This note describes the main factors that influence the relative sensitivity factor (RSF) of a mass spectrometer and describes how to estimate the RSF for a given molecular species.

Mass Spectrometer

Figure 1 shows the major components of a quadrupole mass spectrometer. Typically the gas sample is admitted via an inlet system to the ion source, where it is converted to ions by electron-impact. The ions pass through a mass analyser, and then to a detector. A general introduction may be found in [1].

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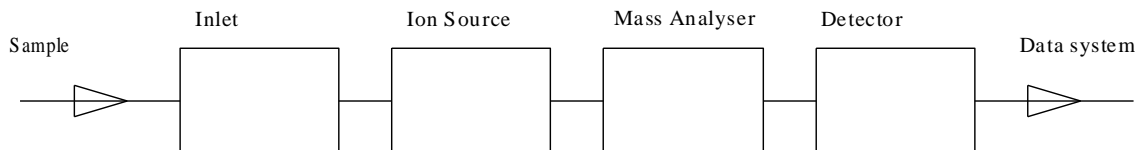


Figure 1 Mass Spectrometer Schematic

The sample is typically a gas. It will probably be at a pressure much higher than the operating pressure of the mass spectrometer, so the inlet system will incorporate pressure-reducing means, such as an orifice, a capillary or a leak valve. Fractionation in the inlet system can affect the performance of the instrument; this can be minimised by correct inlet design [2].

In the ion source, energetic electrons (70 eV) bombard the sample, forming positive ions. Often the sample will break into smaller fragment ions. This gives rise to the “cracking pattern” (or “fragmentation pattern”) of ions formed from a particular molecule. The cracking pattern is influenced quite strongly by the kinetic energy of the ionising electrons, but there will also be variation from one design of ion source to another, and also variation due to factors such as mechanical tolerances and surface condition. Nevertheless, standardised cracking patterns will usually provide a good guide to performance.

Another factor is the transmission of the mass analyser. For a quadrupole, the transmission tends to reduce at higher masses. Usually the transmission can be regarded as effectively constant in the mid-mass region, say from 20 to 50 amu. It is likely to be significantly higher for the lowest masses - perhaps by a factor of two for H₂ at 2 amu and He at 4 amu. At higher mass a power law such as M⁻¹ or M⁻² is sometimes quoted, but this should be applied with caution because there is considerable variation from one instrument to another.

For a Faraday detector the sensitivity does not vary significantly with mass, but the sensitivity of an electron multiplier reduces as the mass increases, typically as M⁻¹.

Relative sensitivity factor

Evidently the instrument sensitivity depends on many factors. We can express this as:

$$RSF = R_I \cdot R_S \cdot R_F \cdot R_Q \cdot R_D \quad (1)$$

Where,

- RSF is the overall relative sensitivity factor, assumed to be 1.0 for nitrogen
- R_I is the inlet sensitivity factor
- R_S is the source sensitivity factor
- R_F is the fragmentation factor
- R_Q is the quadrupole transmission
- R_D is the detection efficiency

The inlet sensitivity factor R_I is impossible to predict with any confidence on theoretical grounds. It is perhaps best regarded as constant when attempting to predict the RSF unless specific information is available, based on measurements on the individual instrument or on the known generic performance of the design.

The source sensitivity factor R_S and the fragmentation factor R_F can be estimated from generic data with a fair degree of confidence. These factors are discussed in more detail below.

The quadrupole transmission R_Q and the detection efficiency R_D are strongly influenced by the instrument design so any assumptions made should be used with caution. In the absence of more

specific information, Figure 2 shows the variation in relative transmission to be expected for a typical small quadrupole.

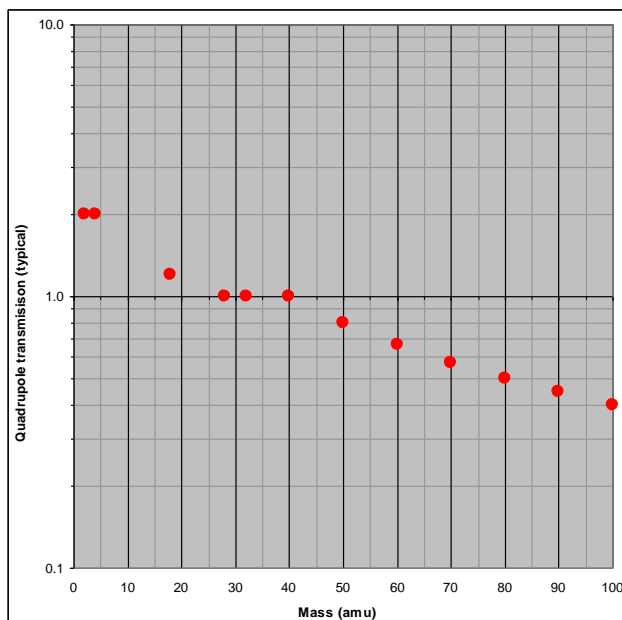


Figure 2: Typical transmission for a small quadrupole mass filter.

RSF in the literature

There is little definitive data in the academic literature relating to RSF for mass spectrometers as such, but there are publications describing RSF for ionisation gauges. There is much in common between the two, because the electron-impact ion source resembles a small extractor ionisation gauge and the basic physical processes that influence ion formation are very similar.

Over the years, many manufacturers have listed RSF data for mass spectrometers in their technical literature, and today one can readily find information on the Internet. It is often not clear whether the data is based on actual measurements on the instruments in question or whether (as is perhaps more likely) the data has been taken from earlier work. Furthermore, it seems likely that the data often originates from measurements on

ionisation gauges rather than mass spectrometers, and therefore will not necessarily incorporate all the factors mentioned above.

Nevertheless, there are useful references, and the spread of results reported from several different sources is not so great as to invalidate the use of 'generic' data. It seems reasonable to assume that typical RSF values can be used in the absence of more definitive calibration checks. Figure 3 and Table 1 show averaged RSF values from Leck [3], where data is tabulated from several studies published in the literature [4-6]. These values may be taken to represent RS in equation 1 above.

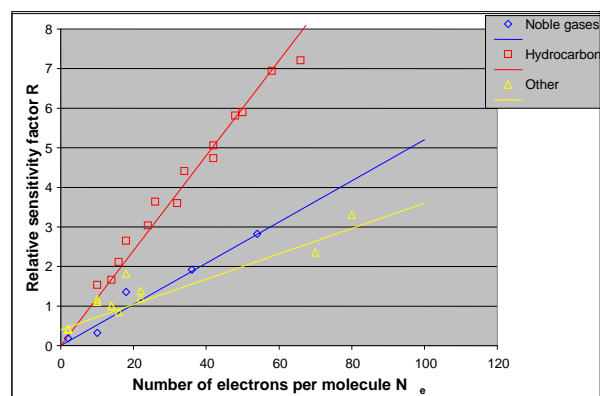


Figure 3: Relative Sensitivity Factor vs No of Electrons.

Helium	0.18
Neon	0.32
Argon	1.36
Krypton	1.92
Xenon	2.82
Hydrogen	0.43
Deuterium	0.40
Ammonia	1.18
Water	1.11
Carbon monoxide	1.01
Nitrogen	1.00
Oxygen	0.85
Hydrogen sulphide	1.82
Carbon dioxide	1.38
Nitrous oxide	1.20
Sulphur hexafluoride	2.35
Mercury	3.30
Methane	1.53
Ethane	2.65
Propane	3.92
Butane	4.42
Pentane	5.06
Hexane	5.90
Heptane	6.94
Iso-octane	7.21
Acetylene	1.66
Ethylene	2.11
Propene	3.04
Butene	3.60
Hexene	5.81
Benzene	4.74

Table 1: Relative sensitivity factors R_s for ionisation gauge

Note that along the x-axis of Figure 3 is plotted the number of electrons per molecule. This has been found to give a reasonable correlation with measured data, and suggests plausibly that the probability of ionisation taking place is proportional to the number of electrons in the sample molecule. Clearly there are other factors at work as well, but the correlation seems quite convincing for the noble gases and for hydrocarbons. The “Other” points fall above the general trend are for ammonia and water (at $N_e = 10$) and for hydrogen sulphide (N_e

= 20). Many other common gases fall close to the yellow trend line.

These values are a good guide to the variation in sensitivity that can be expected from the ionisation process, and thus can be used as an estimate of the source sensitivity factor R_s .

For many common gases the fragmentation factor can be ignored because the base peak corresponds to most of the ion current. For larger molecules with a richer mass spectrum (eg hydrocarbons) this is no longer true, and one needs to make allowance for fragmentation. For example, propane has a base peak at mass 29, but it corresponds to only about 30.2% of the total ion current. Therefore when estimating the RSF we would take the figure for ion gauges (3.92) and multiply it by 0.302, giving us an overall RSF of 1.27. To some extent, the increased sensitivity from the electron configuration is compensated by the reduction due to fragmentation. Even in this case where there is significant fragmentation we would introduce relatively little error if we simply assumed the RSF to be 1.0. In practice, it is often appropriate to ignore the variation in RSF altogether. For the best precision there is no substitute for performing routine calibration check, preferably using a gas mixture whose composition is close to the composition expected from the sample.

Measured RSF

Table 2 shows RSF values from measurements made at Hiden Analytical on a few common gases on a QIC system. Data is shown for a mixture of 2% He, Ne, Kr in N_2 . Ar was not included because of the interference between Ne^+ and Ar^{++} at mass 20

RSF	Measured	Conc.	Literature average and range
H ₂ /N ₂	1.01	2.5%	0.46 (0.33 – 0.70)
He/N ₂	0.27	2%	0.16 (0.13 - 0.25)
Ne/N ₂	0.25	2%	0.26 (0.22 - 0.30)
Ar/N ₂	1.39	50%	1.24 (1.11 – 1.42)
CO ₂ /N ₂	1.00	50%	1.36 (0.90 – 1.54)
Kr/N ₂	1.47	2%	1.76 (1.00 - 1.95)

Table 2 Measured RSF values

For Ne and Kr the measured RSF is quite close to the literature average. The result for He is high, but is only just outside the range of the literature, and is probably influenced by increased quadrupole transmission at low mass.

Also tabulated are measurements of H₂/N₂, Ar/N₂ and CO₂/N₂ using mixtures set up using a gas blender. The measured RSF for H₂ is somewhat higher than the spread of values found in the literature, again probably because of the quadrupole transmission.

Estimated RSF

It is preferable to measure the RSF, but this may not be feasible. In such a case we can estimate the RSF for a particular species as follows. We find the value for R_S from Table 1, and multiply by factors R_F to allow for the fragmentation and R_Q to allow for quadrupole transmission. (Figure 2). The values for R_F are derived from standard tabulations such as [7] or (He, Kr, Xe) from isotopic abundances. The values are normalised to the value for N₂. Data for common gases are listed in Table 3.

	Base peak	R_S	R_F	R_Q	RSF
Helium	4	0.18	1.00	2.00	0.39
Neon	20	0.32	0.90	1.00	0.31
Argon	40	1.36	0.88	1.00	1.27
Krypton	84	1.92	0.57	0.52	0.61
Xenon	132	2.82	0.27	0.33	0.27
Hydrogen	2	0.43	0.98	2.00	0.84
Deuterium	4	0.40	0.99	2.00	0.79
Ammonia	17	1.18	0.53	1.00	0.65
Water	18	1.11	0.81	1.00	0.95
Carbon monoxide	28	1.01	0.92	1.00	0.98
Nitrogen	28	1.00	0.94	1.00	1.00
Oxygen	32	0.85	0.96	1.00	0.86
Hydrogen sulphide	34	1.82	0.50	1.00	0.97
Carbon dioxide	44	1.38	0.80	1.00	1.17
Nitrous oxide	30	1.20	0.89	1.00	1.13
Sulphur hexafluoride	127	2.35	0.58	0.35	0.50
Mercury	202	3.30	0.30	0.22	0.23
Methane	16	1.53	0.46	1.00	0.75
Ethane	28	2.65	0.48	1.00	1.35
Propane	29	3.64	0.32	1.00	1.23
Butane	43	4.42	0.40	1.02	1.90
Pentane	43	5.06	0.33	1.02	1.82
Hexane	57	5.90	0.20	0.77	0.99
Heptane	43	6.94	0.24	1.02	1.82
Iso-octane	57	7.21	0.43	0.77	2.54
Acetylene	26	1.66	0.73	1.00	1.28
Ethylene	28	2.11	0.46	1.00	1.02
Propene	41	3.04	0.32	1.00	1.03
Butene	41	3.60	0.36	1.07	1.49
Pentene	55	0.00	0.34	0.80	0.00
Hexene	41	5.81	0.17	1.07	1.15
Benzene	78	4.74	0.49	0.56	1.38

Table 3: Estimated RSF

In Figure 4 we show the measured values from Table 2 together with estimated values from Table 3. There is reasonable agreement except for Kr,

where the measured value is approximately 50% higher than the estimate.

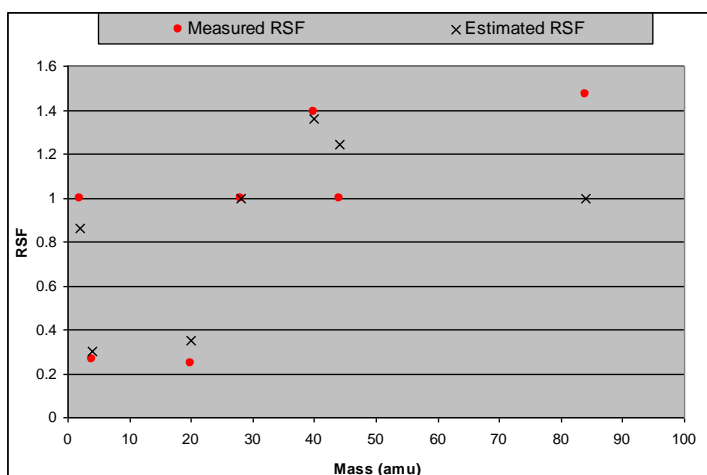


Figure 4: Measured and estimated RSF

Recommendations

Undoubtedly if good precision is required, a regular calibration should be carried out, preferably using a gas mixture whose major constituents are representative of to the expected sample composition.

Failing this, an estimate can be made, as described above. There are many possible sources of variation, but nevertheless such an estimate can be usually good to within a factor of two of the actual value determined by in-situ measurement.

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