Gas Analysis
Application Note 280

Relative Sensitivity

RS Measurements of Vapours

Introduction

Hiden Analytical offers a range of gas analysers suitable for the analysis of gases and vapours. It is often desirable for these analysers to give quantitative as well as qualitative results. The accuracy of these results can depend on the relative sensitivity (RS) value used. RS values are a function of the ionisability of the gas being measured and are typically measured relative to N_2.

The measurement of RS values for permanent gases is relatively straightforward as calibration gas mixtures can be purchased from gas supply companies. Measurement of vapours, however, is more complicated as buying readymade gas mixture is often impossible. In order to calibrate for vapours, some form of vapour generator is typically required.

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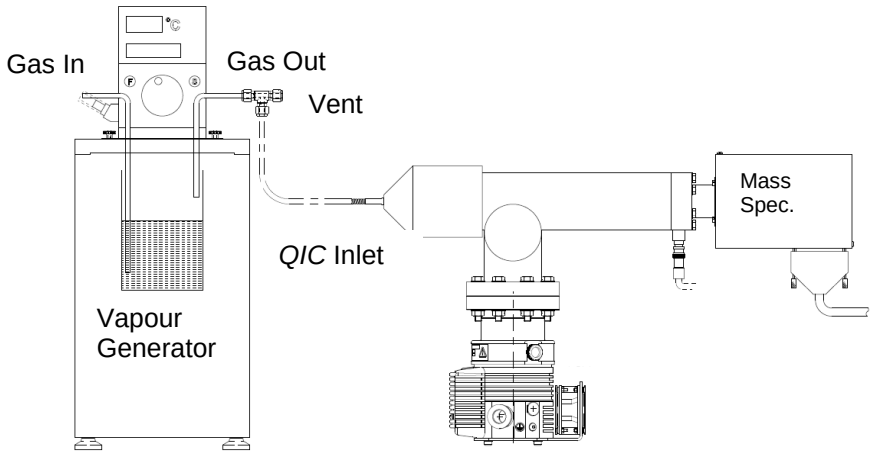

Figure 1 Vapour generator

Experimental

Vapours were produced using a bubbler type humidifier held at constant temperature using a precision, stirred thermostatic water bath, Figure 1. Vapours were transferred using a heated transfer line to minimize condensation between the humidifier and the Hiden HPR-20, Figure 2. The *QIC* inlet of the HPR-20 is heated to 160 °C making it ideal for analysing vapours.

A carrier gas of N_2 was used to generate a flow of vapour through the system. It is assumed that the vapour level is equal to the vapour pressure expected when the liquid is held at a known temperature. Corrections were made for spectral overlaps with N_2 at m/z 28 (methanol and ethanol) before RS values were calculated.

Each liquid was held at three different temperatures in order to generate different vapour pressures. These were used to determine the relationship between vapour pressure and RS value.

Figure 2 HPR-20 Mass Spectrometer

Vapour Species

The following liquids were used to generate vapours at a range of vapour pressures:

Water, 1-3 %

Methanol, 6-18 %

Ethanol, 2-8 %

The differing levels of each vapour analysed represent the vapour pressures that could be generated using the experimental setup.

Results

A plot of the H_2O RS value versus percent H_2O is shown below in Figure 3.

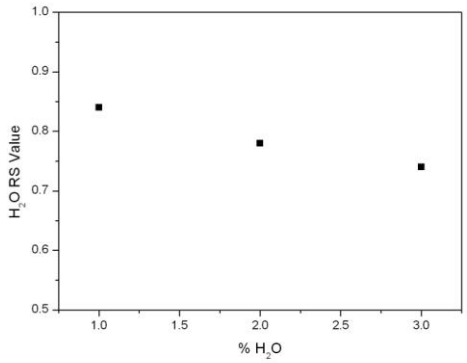

Figure 3 Plot of H_2O RS value vs. % H_2O.

The results of the water experiment give an RS value of 0.79 ± 0.05.

A plot of the methanol RS value versus percent methanol is shown below in Figure 4 below.

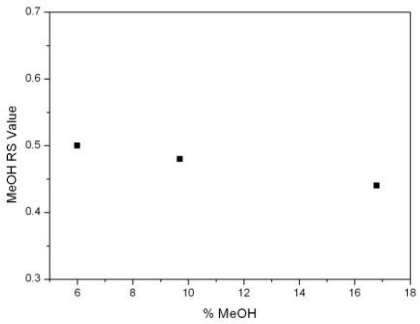

Figure 4 Plot of methanol RS value vs. % methanol.

The results of the methanol experiment give an RS value of 0.47 ± 0.03.

A plot of the ethanol RS value versus percent ethanol is shown below in Figure 5 below.

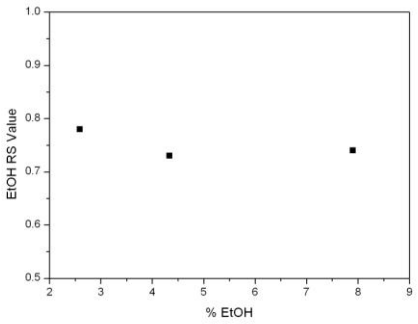

Figure 5 Plot of ethanol RS value vs. % ethanol.

The results of the ethanol experiment give an RS value of 0.75 ± 0.03.

Comparison of the results with literature values for the RS of the selected species shows some differences, see Table 1.

Vapour	Literature RS Value*	Measured RS Value
H_2O	0.90	0.79
Methanol	1.70	0.47
Ethanol	2.04	0.75

Table 1 Comparison of literature and measured RS Values

Table 1 shows the measured results can be markedly different from literature values, except for water. This difference may arise from the fact that literature values are often obtained from the total ion current measured by ionization gauges. Here, the ion current generated in the ion gauge includes a proportion due to the ions generated in the fragmentation of a molecule when ionized. This is not accounted for in the measurements of RS values in mass spectrometers as these are able to select discrete ions or fragments for measurement. Therefore, this shows the limitations of using literature RS values.

Conclusions

As can be seen in Figures 3-5 the RS value decreases with increasing concentration. This could be due to a number of factors. One of the reasons may be a limitation in the generation of the vapour i.e. the assumption that the correct vapour pressure is being generated is incorrect. However, the results show that the RS value is relatively consistent over the measured ranges.

The difference between the measured values and the literature values emphasizes the importance of calibrating the instrument at levels likely to be seen during an experiment if quantitative measurements are to be performed.

* Literature values taken from :

1. R. Holanda, J. Vac. Sci. Technol., 10, 1133-1139, 1973

2. F. Nakao, Vacuum, 25, 431-435, 1975

3. J.E. Bartmess & S.M. Georgiadis, Vacuum, 33, 149-153, 1989