Calibration effects during natural gas analysis using a quadrupole mass spectrometer

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Quadrupole mass spectrometry (QMS) is regularly used for online monitoring of gaseous systems. With the advent of miniature QMS, it is possible to apply this capability to the analysis of gas samples extracted from drilling mud during exploration and development of oil and gas fields. QMS analysis can provide rapid compositional data for a range of hydrocarbons, providing early recognition of potential development issues. We investigate characteristics of QMS systems affecting calibration accuracy.

Keywords: Calibration; Mud gas; Natural gas; Online; Process control; QMS; Quadrupole mass spectrometry; Quantitative; Residual gas analyser; RGA

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1. Introduction

In mass spectrometry (MS) terms, ‘‘mud-gas’’ samples are complex, containing numerous overlapping hydrocarbon species as well as atmospheric contamination. Currently, mud gas is continuously sampled and analysed at the surface by low-resolution gas chromatographs using flame-ionisation detectors (FIDs), providing only semi-quantitative assessment of hydrocarbons with carbon numbers 1–5. Such data can be interpreted to give very early indications of oil or gas compositional heterogeneity within petroleum reservoirs and, combined with other data, help confirm the presence of fluid-flow barriers that may impact on recovery and hence field economics.

QMS is commonly employed in residual gas analysers (RGAs) as a cost-effective way of monitoring and controlling systems down to a detection level of parts per billion (ppb). Limiting factors for portable instruments are now decreasing with software making them easy to use, bringing about an increase in the number of applications and uses. Demand for increased speed of analysis has regenerated interest in multivariate or chemometric methods for MS, so direct sampling methods can be employed, removing the requirement for a front-end separation technique. These methods are already commercially employed for QMS-based e-noses (e.g., MS-200, Kore Technology [1] and Chemsensor 4440, Gerstel GmbH & Co. KG).

Despite being a well-established technique, absolute confidence in QMS for quantifying gaseous species is limited. Accuracy of these measurements will depend on calibration frequency for both univariate and multivariate methods. For multivariate methods, signal drift is an issue and creates deviations from the initial calibration model. To overcome this drift, normalisation methods are employed to the sum of peaks, base peak or to an internal standard.

This article investigates the cross sensitivity of a species and how exposure to one gas changes the response of the instrument to a second gas. Such effects will have effects on multivariate calibrations and raise questions about the accuracy of internal standards employed in QMS systems for mud gas and any other online applications. Direct sampling quadrupole MS (DSMS) is a cheap, easy method for analysis of gaseous systems. Introduction of gases into the vacuum system is via a capillary inlet or, for higher sensitivity, a membrane inlet. An account of theory of QMS systems can be found [2].

QMS technology has many potential applications within the petroleum industry (e.g., the analysis of gas samples extracted from drilling mud, which is used to clean, lubricate and stabilise boreholes within oil or gas fields [3]). During the exploration and development of oil and gas fields, mud-gas data provide basic characterisation of

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in-reservoir compositional heterogeneities that are common to many oil and some gas fields [4,5]. Mud-gas analysis complements traditional methods, which identify in-reservoir compositional variations using detailed organic geochemical analysis of petroleum samples, extracted from the reservoir during testing [6]. Reservoir geologists/engineers can use the presence of compositional heterogeneities to help infer the presence of fluid-flow barriers that may impact on petroleum recovery and field economics. Recently, miniature QMS systems have been fabricated using microengineering techniques and these are approximately an order of magnitude smaller that conventional systems [7]. It is therefore feasible to perform QMS analysis in the harsh environment downhole in an oil/gas reservoir. This removes the problems associated with atmospheric contamination and potentially provides better quality mud-gas data with which to characterise in-reservoir heterogeneities.

DSMS using QMS has its measurement issues; non-linearity and stability are sources of uncertainty. Overlapping analyte fragments at similar *m/z* values can make definite species identification problematic. These problems have led to the instrument being used in only a semi-quantitative manner with a limited degree of accuracy. The focus here is measurement quality and the effect of the factors that may change instrument response. Such characteristics need to be accounted for before application of chemometric methods.

2. System conditioning and optimisation

A QMS detector may be either Faraday cup or electron multiplier. The Faraday cup has a minimum detectable pressure between 10^{-10} and 10^{-13} Torr; with a multiplier, pressures of 10^{-15} Torr are detectable. Resolution and sensitivities depend very much on the operating parameters, such as the ion energy and electron emission of the source. These operating parameters and the history of use may also alter the linearity of the detector response. It is further reported that linearity changes with the make of instrument, as it can vary from just high-pressure non-linearity to non-linearity for all combinations of the operating parameters. It is stated that, at best, after correct calibration, these instruments are accurate to a few per cent [8]. The dependence of detector stability on analyte gas for non-active gases gives a drift of as little as 10% over a period of months. There are reports of changes in the region of 10s of % using a Faraday detector over the period of one month and a factor of 5 over 10 days when an electron multiplier detector is employed [9]. Long-term sensitivities of five commercial QMS systems to one non-active gas, argon, varied between 30% and again a factor of 5 [10].

The method of ionisation to be used here is the commonly employed electron impact. Electrons are emitted from a hot filament and collide with the sample; ionisation and fragmentation occur. On switching on the filament, an increase in pressure is observed as a result of outgassing of the filament. In a well-degassed QMS system, the outgassing effect does not occur when switching the filament on, although the spectrum can vary initially.

Currently, the level of atmospheric contamination in surface-based mud-gas analysis is of the order of 90+%. To quantify accurately components in this scenario requires quantitative component analysis at the sub-1%-ppm level. This would require calibration for many minor constituents that are of little or no interest. Downhole analysis would virtually remove air contamination such that a 1% level indication would be satisfactory. This would enable a Faraday detector to be employed, thus reducing both the calibration requirements and the frequency of recalibration, as it is a more stable detector.

Recommended calibration and operation procedures have been discussed previously [11]. Several hours are suggested for the sensing head/ion source to stabilise and a period of 6 h following bake-out at 350–400 °C to allow for the system to cool down suitably. From initiation of the vacuum system, over 24 h are required to obtain ultimate base pressure and stability. These effects can act as limiting factors when trying to deploy these instruments quantitatively in harsh environments, as power supplied by battery systems is limited, and preconditioning prior to deployment would be recommended.

3. QMS and chemometric methods

Mathematical methods to provide both qualitative and quantitative information from mass spectra have been around for a considerable time. Often, these methods rely on the resultant measured spectrum being linear combinations of pure components. In this case, pure spectra can be multiplied by the relevant concentrations to give the best fit to the sample spectrum and thus a quantitative estimate of the components present. Earlier work found that, if the sample contained one or more unexpected components, then considerable errors were noted [12]. Least squares methods were employed utilising as many as 110 masses with no pre-selection. Early work on factor-based methods has also been described [13–15], and more recent work employs an algorithm that adds additional complexity to the calibration and takes into account differences in diffusivities across the sample membrane to distinguish between components [16]. Chemometric methods for DSMS have been assessed [17], comparing univariate least squares (uLS), partial least squares (PLS) and also second order methods tri-PLS and parallel factor analysis (PARAFAC), which again utilise time-dependent effects. A comparison of the common chemometric methods, classical least squares (CLS), inverse least squares (ILS) principal component regression (PCR) and PLS has been assessed [18]. Other earlier work included not only quantifying components but also library-matching systems that are routinely employed in gas chromatography–MS (GC–MS) systems. Normalisation of spectra enables comparison summation of the peaks to unity that can put unequal weighting on the largest peaks in the multivariate methods. The smaller peaks can be as important as the larger ones when discriminating and quantifying the components [19]. This pre-processing of spectra will be an important factor in the results of a multivariate calibration.

4. Methods of drift correction

Characteristics of quadrupole systems make it difficult to employ straightforward chemometric methods for on-line analysis. The drift in the system has to be corrected and accounted for prior to employing a multivariate method. Methods to do this have been explored. Drift in QMS signal could simply be multiplied by a factor to correct the signal to its original intensity at the point of calibration [20]. This would require a second calibration and extrapolation. This also raises the questions of the extent of recalibration and whether a partial calibration be employed (i.e., whether the change in response of one gas be used to characterise the change in response to a second).

Pulsed gas-sampling systems have been investigated to correct MS drift [21]. The use of standard gas additions (SGAs) has also been explored by Pérès et al. [22] who utilised a helium–xenon mix (98:2) that is constantly bled into the system via a capillary at 0.2 ml/min. The SGA addition was compared to internal normalisation and showed an improvement on subsequent PCA analysis. SGA does add problems with respect to system portability and cost; the gas flow could be reduced and the percentage composition of the standard gas increased to minimise the volumes of standard gas required. However, the effect of active gases (CO_2, O_2, CO, CH_4) on the response of inactive gases (N_2 and noble gases) may make the use of SGA additions application-dependent.

5. Experimental set-up

Two commercial QMSs were used to ensure that the results can be regarded as a generic feature of QMS instruments and not just limited to one design or particular model. The models used for experimentation were the MKS Microvision plus and the Pfieffer QS422. The vacuum system was set up so that inlet systems were opposite the vacuum on a six-way cross. The distances of the ion sources from the inlets and the pressure gauge were arranged to be as equal as possible. Two total pressure gauges were used for these tests: a Leybold ITR 90 or Pfeiffer PKR 251 (operated and controlled via the quadrupole software). Both are gas-specific, and conversion factors were employed for the appropriate gas (0.8 argon, 1.0 nitrogen) The error margins on such gauges are within ±15%. Inlet 1 comprised a capillary with a bypass fitted. The bypass vacuum was provided by a second rotary pump, minimising disturbance to those providing the system vacuum. A valve was also used to switch off capillary intake. Inlet 2 was a needle valve, allowing variable amounts of sample into the system and thus control of operating pressures.

The system was up and running for five days prior to measurement and, throughout this period, the system was baked for a total of 24 h. The filaments were switched on 24 h prior to measurement to ensure filament effects on the resultant spectrum were minimised. A final base pressure of 3×10^{-7} mbar was achieved.

On opening the capillary inlet, an operating pressure of approximately 4×10^{-6} mbar was obtained. Thus, the analogue scan of the base pressure should contribute 7.5% of the sample spectrum. For the tests in Fig. 3, the capillary was sampling from a flow of methane at 200 ml/min and was set using mass-flow controllers (MKS 1179A, 1 slm), which have an error of ±1% of full range (±10 ml/min). The intake along the capillary is in the order of 20 ml/min. As it is sampling from a constant flow to atmosphere, the input into the instrument is regarded as constant. The sampling pressure, being far in excess of the system operating pressure, determines the flow, and the effect of fluctuations of pressure variations in the vacuum system can be ignored. Gases used were argon (Pureshield BOC 99.997%), nitrogen (Linde Gases 99.997%), oxygen (Linde Gases 99.5%) and methane (Linde Gases 99.95%).

6. Results and discussion

6.1. Least squares determination

Table 1 shows a natural gas mixture (actual concentrations provided by the UK National Physics Laboratory using thermal conductivity and flame-ionisation methods). The pure components were individually measured on the same day as the natural gas sample. Spectra were taken with no pre-processing in their analogue-recorded format and were recorded using an electron multiplier detector. It can be seen from Table 1 that the calibration was successful; depending on the operator's requirements, a percent level indication may be satisfactory, but, in other circumstances, trace elements may be of importance and this level of calibration would be insufficient. CO_2, N_2 and CH_4 were overestimated; the other components were all underestimated.

Table 1. Ordinary least squares (OLS) determination of the components present in natural gas, estimated by recording pure components (Sigma–Aldrich)

	Actual concentrations (%)	**Calculated concentration (%)**
Carbon dioxide	1.31	1.64
Nitrogen	0.93	1.65
Methane	91.85	92.74
Ethane	4.48	3.01
Propane	1.09	0.69
n-Butane	0.20	0.04
Iso-butane	0.13	0.23

Results may be improved by pre-processing data or by developing multivariate or chemometric methods. Development of chemometric methods is not the focus of this article, although the areas of interest are the factors that may lead to inaccuracies when applying chemometric methods.

6.2. Base pressure

The base pressure in the region of 3×10^{-7} mbar and a capillary inlet giving an operating pressure of 4×10^{-6} mbar means that the base-pressure spectrum is still a substantial part of the sample spectrum. This can be simply subtracted from the sample spectrum. However, for online processes, there will be fluctuations in the base pressure, particularly if measurement is required in the first 24 h after system start-up. A problem for portable QMS systems is their limited time for stabilisation because current battery life and power requirements give a limited operating period. The result is a degree of inaccuracy in the base spectrum. The composition of the base spectrum could also change as a result of the operating environment. If the instrument is deployed down a drill hole, then it is likely that the base spectrum will not resemble that from an air sample. It is worth noting that operating at a higher inlet pressure will reduce inaccuracies as a result of base-pressure changes.

6.3. Tracing changes in instrument sensitivity using standard gases

A mixture of neon (85.9%), propane (13.1%) and xenon (1%) (NPX) was used to map instrument performance with a secondary electron multiplier (SEM) detector. The instrument was not dedicated to these experiments and would have had a variety of other uses, as would an instrument employed in the laboratory. Fig. 1 displays the percentage change in signal over a period of 12 months. From 6 months onwards, identical ion source and detector settings were used but did not bring about signal stability. Changes of 100s of % were observed. Xenon was not admitted to the instrument via an independent inlet. The change in instrument response to xenon and the other components was seen to be very different at between 8 and 12 months. If the xenon was used to correct the instrument drift, the result would be inaccurate, the differences cannot be accounted for by atmospheric contamination as an enclosed system was used.

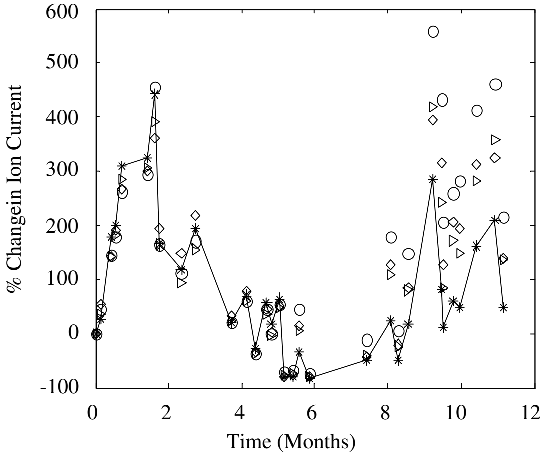

Figure 1. Percentage change in signal intensity of a standard gas mixture of neon, xenon and propane was recorded on a regular basis over a 12-month period using a SEM detector ▷, *m/z* 44; ◇, *m/z* 20; ○, *m/z* 28; ∗, *m/z* 129 (xenon).

In the analogue spectrum of the NPX mixture, the base peak was mass 20 (neon). This was also seen to be changing in ratio to the other compounds present. Normalising the spectrum so the base peak was equal to 1 would be incorrect because the other peaks are not changing in the same way. Normalising to the total ion current estimated by summing the peaks has not proved successful. Histogram or analogue modes are required for this type of normalisation, but, depending on the QMS scan rate, partial pressures may change during a scan. An external pressure gauge would correct for pressure but not discrete changes in detector drift or changes in the ion source degradation.

6.4. Cross-sensitivity effects

We examined here the effect of an active gas (CO_2) on a constant partial pressure signal of methane (mass 15) on two different commercial QMS systems. Fig. 2 shows the mass 15 signal before and after exposure of the QMS system to CO_2. In this case, the inlet system comprised a series of controlled leak valves with a 1-litre sample reservoir. A manifold and second rotary pump controlled the pressure.

Methane was admitted to the vacuum system, giving a total pressure reading of 9×10^{-7} mbar as measured on the gauge. On admitting the CO_2, the total system pressure increased to 9×10^{-6} mbar and the mass 15 signal increased by about 25%. We noted that mass 15 is not subject to overlapping peaks from fragments of other compounds present.

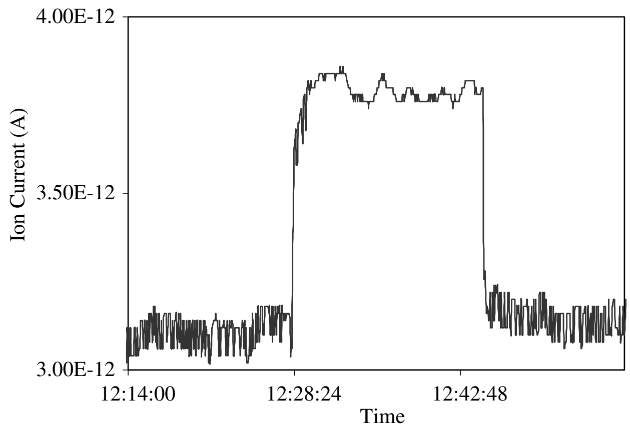

Figure 2. Constant partial pressure of methane (*m/z* 15), following exposure to carbon dioxide.

Fig. 3 also shows a constant signal of methane at mass 15, for the Pfeiffer QMS using a different inlet mechanism. In this case, methane was introduced through a capillary and then a second gas (N_2, Ar_2 or CO_2) through the valve inlet. The methane pressure reading was 3×10^{-6} mbar and, with the second gas, an operating pressure in excess of 2×10^{-5} mbar was obtained. Both non-active gases also increased the sensitivity of the m/z 15 signal peak. The partial pressure of the methane remained constant and this was not reflected by the observed increase in the m/z 15 signal.

The signal increase in this case could be brought about by the removal of absorbed species, effectively re-conditioning the analyser or detector, resulting in the observed increase in transmission of the ions through the mass filter or increased detection. This has been previously reported for He:Ar mixtures [10].

The mass-15 response following exposure to the active gas (CO_2) gives a very different trace with the m/z signal taking time to plateau following admission of CO_2 into the system (Fig. 3, lower trace). Post exposure to CO_2, a recovery time is observed. The magnitude of these effects is related to pressure. Further investigation requires the use of a pressure sensor that is not specific to any particular gas.

6.5. Cross sensitivity at constant pressures

In monitoring situations, it is unlikely that there will be such an exaggerated change in operating pressure as discussed in Section 6.2. However, if sampling takes place from a process stream, a build-up of gas pressure in the sample inlet could be frequent and the effect of this on QMS calibration needs to be considered.

Assuming that the operating pressure in the vacuum system does remain constant, the effect of a change in composition of the sample-gas intake through the inlet needs to be considered. Fig. 4 (upper) shows a process stream of constant flow, the composition of which is controlled using mass flow controllers to alter the percentages of the components. Argon gave a reasonably linear response, as the percentage flow of argon increased when nitrogen was the balance gas; when the nitrogen was replaced by methane, the difference to the argon response was not significantly different.

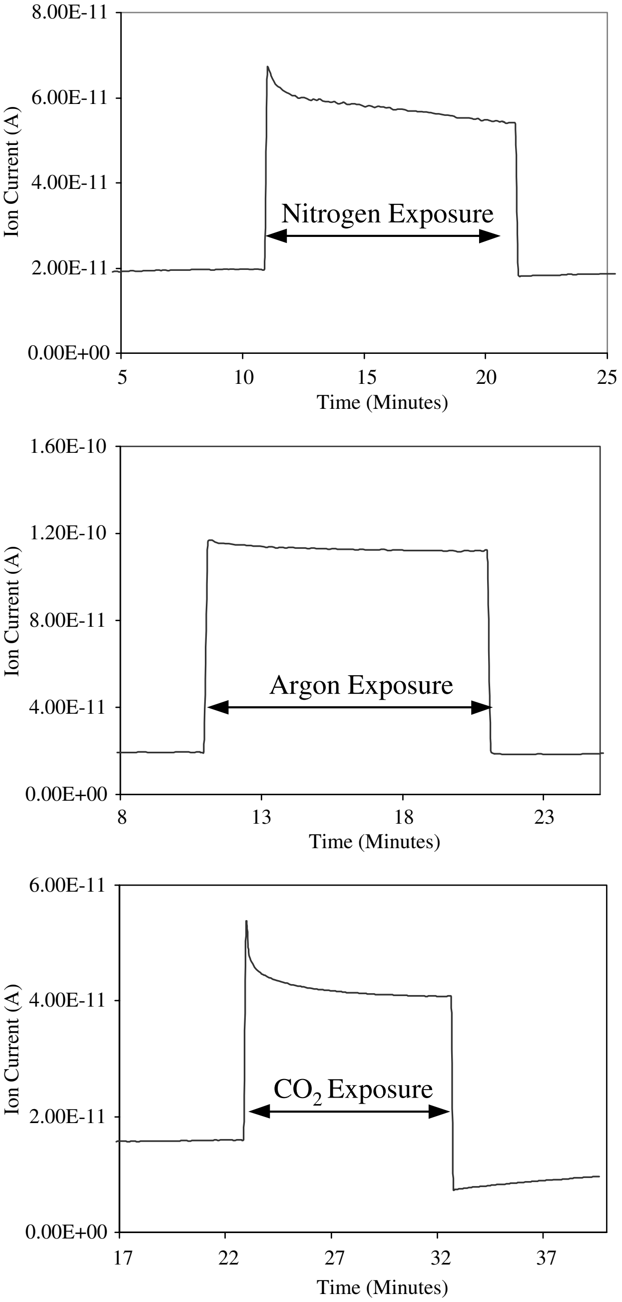

Figure 3. A constant partial pressure of methane was provided via a capillary inlet (4×10^{-6} mbar). The total pressure of the system was then increased by opening a valve inlet ($>2 \times 10^{-5}$ mbar). Here, methane (*m/z* 15) signal intensity is observed on exposure to inactive gases (nitrogen and argon) and an active gas (carbon dioxide).

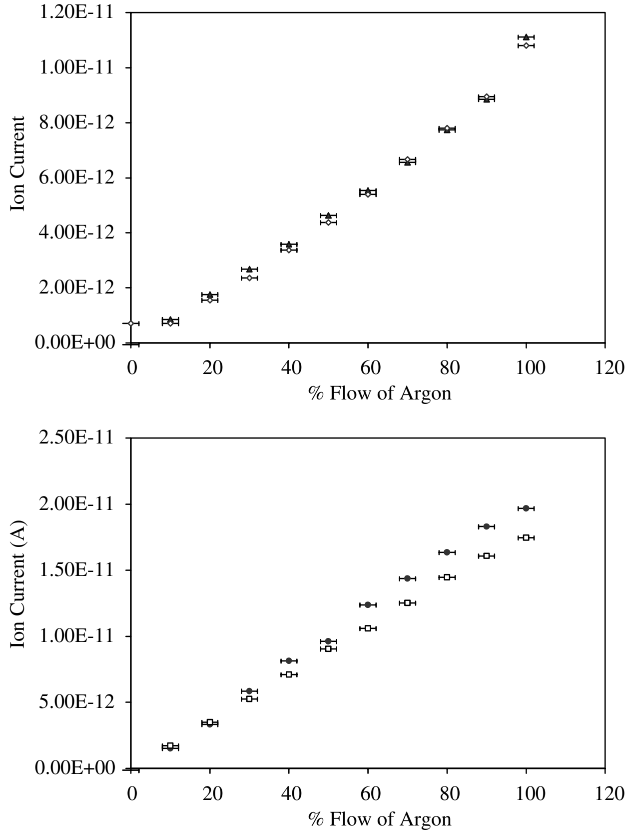

Figure 4. Gas is introduced into the vacuum system via the capillary. The capillary is sampling from a flow of 500ml/min; the composition of the flow is set by mass-flow controllers. The balance gases above are: ▲, methane; ●, oxygen; □, argon; and ◇, nitrogen.

The methane (*m/z* 15) peak was analysed in a similar manner. Methane response with oxygen as a balance gas was compared to the percentage flow of methane with argon as a balance gas. We noted a slight separation in the responses.

7. Conclusions

Confidence in QMS for quantitative work is currently limited. Little use has so far been made of multivariate methods to resolve overlapping fragments. The limitations of QMS arise from deviations from signal linearity with pressure, interference and memory effects to give non-linearity over percentage composition ranges.

Normalisation methods are frequently employed with the aim of removing variations in operational pressure, degradation in the detector and ionisation efficiency. Long-term monitoring of neon, propane and xenon showed that normalisation of the base peak (Ne) equal to 1 is of questionable value. This also highlights that the long-term change in instrument response to one compound (Xe) is not necessarily the same as the change in response to a second compound. For the same reason, long-term employment of single gas standards as a suitable method for drift correction is also questionable.

The cross sensitivity of methane (*m/z* 15) to active gases (CO_2) and also inactive gases (N_2 and Ar) and has been shown. Currently QMS operational pressures are in the region of 10^{-6}–10^{-5} mbar. QMS systems tend to be relatively stable within this region and the cross-sensitivity effects as a result of large pressure changes are thus minimised. In many cases, it is beneficial to operate at high pressures. However, if cross-sensitivity effects result from surface charging/absorption/desorption, then higher pressures may exaggerate these memory effects, and this will need to be considered in future instrumentation systems.

These results demonstrate that, if a QMS system is to be employed for quantitative natural gas analysis, it is best to avoid atmospheric contamination. Oxygen and carbon dioxide will have only negative effects on any calibration scheme employed.

Exclusion of atmospheric contamination can be achieved by miniaturising QMS systems and implementing downhole analysis. In downhole monitoring, the natural gas component in the mud-gas sample greatly increases, and this reduces detection-limit requirements; this enables less sensitive, but more stable, Faraday detectors to be employed, and further simplifies calibration requirements. Miniature and micro-QMS instruments are set to play an increasingly important role in harsh environment MS.

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