

T H E U S E O F T E S T G A S E S

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DANTEST

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Introduction

I have been asked to talk about the certification and use of test gases. With Torbjørn Nilsen talking about production and certification of test gases, I shall try to talk about test gases from the viewpoint of the user, as well as my experience as an analyst with test gases.

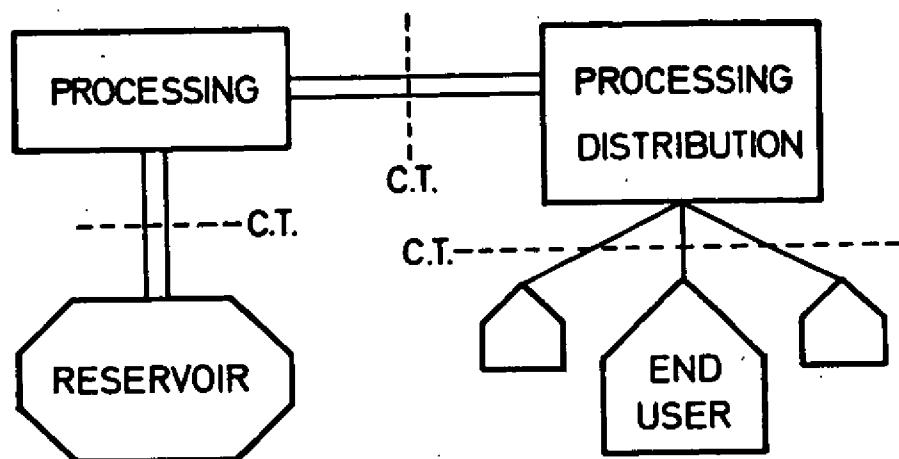
I shall not talk very much about certification, because the most accurate test gas that can be produced is a gas that has been prepared by the gravimetric method. There is no way to add accuracy to such a gas by analysis, the only thing that can be added is confidence. Of course it is possible to certify a gas by analysis, but the use of this gas will be limited to places where less than the best accuracy is acceptable.

I have relied rather heavily on the Gas Quality conference (1) that was held in April this year in Groningen because test gases and gas quality are closely connected. Actually whenever a quality parameter is measured, test gases have been used at some stage or another in the measuring process. A quality parameter is a parameter that depends on the composition of natural gas.

By test gases is here meant synthetic natural gas mixtures that could be used for gas chromatographic analysis of the main constituents in natural gas. Trace components like water and sulphur compounds are important in gas quality specification, but their analysis is very specialised. Besides there are several independent methods for the analysis of most of the trace components and some of these methods do not need test gases for calibration.

Why is it we use test gases? Well, it is primarily because some measurements can only give quantitative results by calibration with gases of known composition. Furthermore test gases are needed as part of the quality assurance program as a convenient way of convincing oneself and others that the measurements are as accurate as they can possibly be.

In order to get some perspective I have made this simplified picture of the natural gas world. There is a gas reservoir with a pipeline to a processing unit, that removes unwanted components, like water and condensate. Another pipeline brings the gas to the distribution system, where it again may be processed, odourised for instance. Finally the distribution system brings the gas to the end user, who will typically burn it.



The natural gas world. C.T.: possible custody transfer points.

At several points in the system there may be custody transfer. Whenever there is custody transfer two questions must be answered: How much gas is there? and How good is it?.

The answer to "how much" is generally expressed in cubic meters at some reference pressure and temperature. The answer to "how good" is primarily a statement of calorific value, but may also refer to the absence or low level of for instance sulphur compounds.

Measurements on natural gas.

There is a desire from all parties involved that the properties are measured precisely and with a negligible bias.

The measurements may be absolute or relative. An absolute measurement is a measurement with an unbroken line of traceability to the fundamental units of mass, length, current or time. A relative measurement lacks one or more links in the traceability train (2).

The gaps in the traceability train for relative measurements may conveniently be overcome through the use of calibration standards which for our purposes means test gases.

While absolute measurements are more simple to understand, the relative measurements may be much more feasible, faster and even more accurate. Let me illustrate this postulate by two ways of measuring the density of natural gas. Density is by definition the mass of a unit volume of a substance. Thus the density may be found by weighing a known volume of natural gas at a given pressure and temperature in a suitable container. This is an absolute measurement, but it is not feasible outside a laboratory. Instead the choice can be to use a density transducer, which has to be calibrated with test gases.

Gas chromatography

A gas chromatographic analysis is a relative measurement, so the analysis will have an uncertainty that is a combination of the uncertainty in the reference gas used and the precision of the equipment. Error in the composition of the reference gas will be a major source of bias in the measurement.

In view of its importance I have allowed myself to repeat for you some of the properties of gas chromatography.

Elements of a gas chromatograph

- Carrier gas
- Sample size
- Column
- Column oven
- Detector

The carrier gas brings a portion of the sample to be analysed to the separating column, where the different compounds are delayed more or less so that groups of compounds will reach the detector at different times. With gas chromatography of complex mixtures like natural gas it is important to know before an analysis is made, which compounds the sample should be analysed for and what the expected concentrations are.

Each choice of element in the system optimises analysis of some compounds while others may not at all be detected. The carrier gas most often used is helium, and it is excellent for the purpose except for analysis of helium or hydrogen contents. The sample size is chosen with respect to the expected concentration of the compounds of interest: small samples are used for compounds in the percentage level larger samples for compounds in ppm level, with a compromise when the ppm compound elutes close to a percentage compound.

The heart of the system is the separating column. The separation depends on the temperature, the length of the column and type and amount of adsorbent or coating. In general low boiling compounds need long columns and low temperatures to be separated while high boiling compounds need shorter columns and high temperatures to pass the column in a reasonable time. By use of column switching with different columns and eventually temperature programming it is possible to overcome some of the conflicts. Columns switching causes pressure pulses and may influence the quantification of peaks eluting shortly after.

There are two detectors commonly used for natural gas analysis: the thermal conductivity detector, the TCD, and the flame ionisation detector, the FID. The TCD is a robust generally useful detector, that responds to anything with

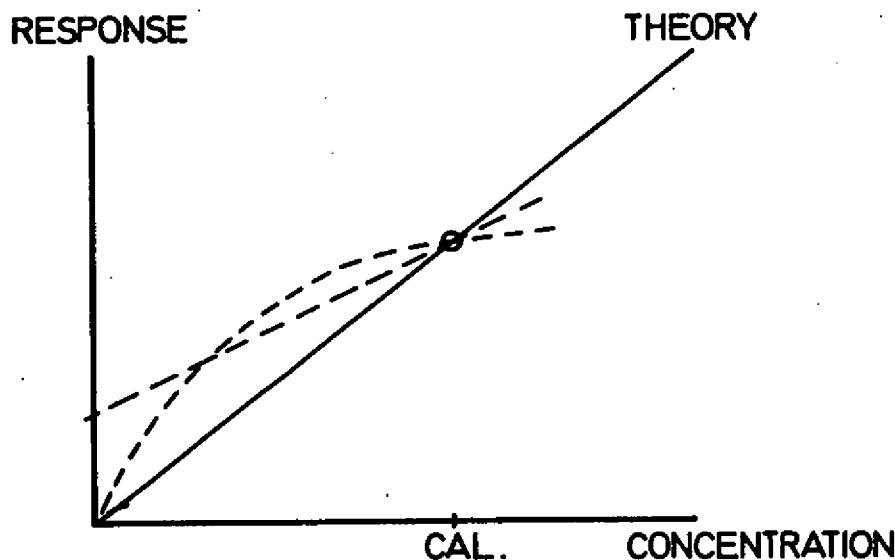
thermal conductivity different from the carrier gas. Except hydrogen everything else has significantly lower thermal conductivity than helium, which makes helium an ideal carrier to use with a TCD, unless helium or hydrogen should be analysed.

FID's are sensitive to essentially all organic compounds and it is orders of magnitude more sensitive to the higher hydrocarbons than the TCD.

Besides these two general purpose detectors there are selective detectors of which the flame photometric sulphur detector is the more common in natural gas analysis.

No matter which detector its response is compound dependent and to get quantitative results it is necessary to use a calibration gas mixture to establish the response factors that shall be used to convert the peak areas to concentrations. Moreover it is essential to treat the calibration gas exactly as the samples are treated, so that the peak shape of each component is the same in both cases.

It is common to use a single calibration gas mixture and assume linearity. Some possible errors in this assumption are illustrated here.



Instrument response as function of concentration of a single component. Dotted lines represent possible deviations from preferred behavoir.

The curved line demonstrates the effects of a saturation phenomenon of the detector. This will primarily happen at high concentrations of the component. The other line has a nonzero intercept due to interference from another component. Such interferences can happen when there is not complete separation of the components. It was mentioned at the Gas Quality conference that one should always determine the full linearity curve for all components. This is a very idealistic approach, and besides being very time consuming, it is not necessary, when one deals with natural gas of pipeline quality. However it will always be wise to have at least two checkpoints to cover the gas compositions that are likely to occur.

Natural gas analysis.

There are several standards (for instance ref. 3,4) for the analysis of natural gas by gas chromatography. They mainly focus on the analysis of compounds of influence on the calorific value. These are the compounds normally found in calibration gases, and the methods of the standards may therefore be used for certification and verification of gas mixtures.

Certification means here that the resulting certificate will contain the "true" concentrations of the constituents. Verification similarly means that the "true" values from a supplier are confirmed by the analysis.

Verification may be performed on a typical natural gas analyser, that can analyse for all the compounds in the certificate, or all except one. The verification should always be done as part of the reception procedure for a new test gas.

There have been two schools for calibration one preferring binary mixtures the other multicomponent mixtures. At the Gas Quality conference Rhoderick and Hughes from NBS presented a lecture on the subject and concluded that there was no difference in accuracy between the two methods (5). Further when there is column switching the multicomponent mixture is a must besides being much more convenient.

Natural gas analysis is probably the only analysis, where one tries to quantify the main component directly as well as all the "impurities". The result is, of course, that the analysis does not sum up to 100 %. To help this one can normalise the results - ISO 6974 allows normalisation when the sum is between 99 and 101 %. Another way is to quantify the methane by difference. In either case the difference to 100 % ends in the methane concentration. Normally this difference is caused by the repeatability of the instrument, but it may also hide the existence of some component not analysed for.

Can test gases be trusted?

In general the answer is yes, no matter who is the supplier, be it a commercial company or some official authority. The latter by definition must be trusted, but anyway, humans are involved in the preparation of the gas and the writing of the certificate. Thus there is always a finite risk that the gas at hand is the one that is off specification. This is the reason a test gas always should be verified before it is taken into use. Bearing in mind that the test gas essentially controls the bias of the measurement, the efforts of verifying it are small compared to the inconveniences an erroneous test gas will cause.

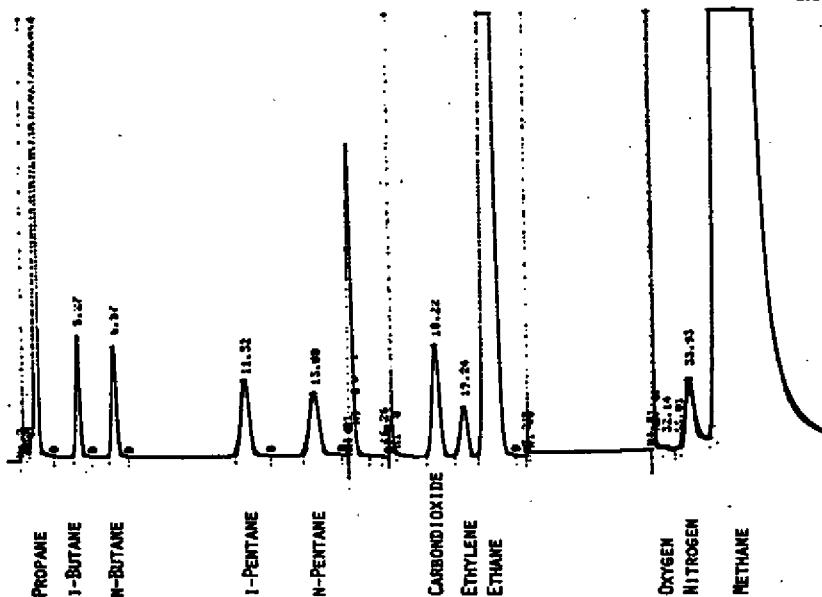
A few years ago the BCR arranged an intercomparison of reference gas mixtures for natural gas (6). Some 16 participants each prepared up to three different gas mixtures of three nominal compositions. Each group of mixture was then analysed by 3 to 4 laboratories. The conclusions from this exercise were that :

- (i) The gravimetric methods for preparing gas mixtures, if they are carefully applied, allow to prepare mixtures of sufficient accuracy.
- (ii) The major source of error seems to be impurities in the primary gases used for the mixture.
- (iii) The main source of error in analysis was the differences in accuracy of the analytical procedure of the laboratories.

Among the impurities found were hydrogen and ethylene. Both are impurities commonly found in gases prepared from refinery gases.

Roughly half of the participants were compressed gas producers, three were independent or governmental laboratories and the remainder were natural gas companies.

My own experience with test gases is limited to around 20 different primary mixtures, and as I mentioned, generally the test gases are as good as they claim to be. This does not mean that I have not seen gases with impurities, on the contrary I can show you this chromatogram which shows traces of ethylene. However, even with the impurities the concentrations of most components have been within the experimental error from the certified values, with discrepancies mainly for the pentanes, that were present in the 0.1 mole % level. Further I have had the pleasure to find that one company, which previously had delivered test gases containing ethylene, now is aware of the problem and uses clean primary gases.



Example of chromatogram of a test gas with ethylene at a level of 0.1 mole %.

References

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