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TRACEABILITY IN MEASUREMENT OF NATURAL GAS QUALITY

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Traceability in Measurement of Natural Gas Quality

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Summary

Flow measurement of natural gas combined with quality determination of the gas (e.g. the calorific value) provides the usual units in which accounts are settled. The concept of traceability in flow measurement is well defined but in the determination of the quality of gas the term traceability has up to now been bypassed because of technical difficulties. During the last two years a lot of work has been done internationally to reach a possible method of obtaining traceable determination of the quality of natural gas. The status of the work done within ISO and WECC will be given and the possible impact on the natural gas industry will be reflected on.

Traceability in measurement of natural gas quality

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1.0 Introduction.

The definition of traceability of a measurement is given in ref. (4) and is repeated below:

Traceability: The property of a result of a measurement whereby it can be related to appropriate measurement standards, generally international standards, through an unbroken chain of comparisons.

Why should this apply to natural gas quality and how can it apply? To answer these questions a quick look into the state of art of obtaining information on the gas quality will be given.

Gas quality is usually specified by the calorific value of the gas. This parameter is defined in ISO 6976 (ref. 3) and can be measured by using for example calorimeters or gas chromatographs. In the last years on-line gas chromatographs have totally dominated the scene in determining the calorific value.

The gas chromatograph determines the molar composition of the gas and by using the calculation procedures described in ISO 6976 the calorific value can be calculated.

Therefore in the following the concept of traceability in measurement of natural gas quality will deal with the traceability of the determination of the calorific value through gas chromatographic analysis.

2.0 Traceability of the determination of the calorific value of natural gas.

A gas chromatographic analysis system comprises a gas chromatograph but equally important reference gas mixtures to calibrate the gas chromatograph. In table 1 is listed a number of parameters that are necessary to take into account in order to achieve an accurate determination of the molar composition of the gas sample.

Table 1 Parameters in the analysis of gas

1.	Performance evaluation of the chromatograph (Linearity, stability, repeatability etc.).
2.	Procedures of analysis.
3.	Correct calibration procedures(e.g. recalibration intervals)
4.	Operator training.
5.	Correct reference gas mixtures for the gas to be analysed, both in compositions and in numbers.

Let us assume that laboratory A and laboratory B analyse the same gas and, although they have fulfilled the demands in table 1 optimally, are getting major deviations on f.ex. the nitrogen content or another very common error contributor: The ethane content. The laboratories go into very costly research and come up with one factor that deviates: The manufacturer of the reference gas mixtures. Laboratory A uses another manufacturer of gas than laboratory B.

The answer to the first question: "Why traceability in the measurement of natural gas quality" is illustrated by this example: If both manufacturers could claim traceability of their reference gas mixtures, deviations as laboratory A and B found, would not be encountered.

In table 2 are listed some of the reasons why traceability is necessary and the importance is no less when laboratory A and laboratory B represent two countries at a major sales junction.

Table 2 Why traceability

1. Avoid costly investigations of the analytical systems.
2. Avoid disputes with costly lawsuits.
3. Ensure reliability of measurement results.
4. To create confidence in measurement results.

Unfortunately not all deviations are detected as easily as in the case of laboratories A and B and this is one of the reasons why the next question: "How to apply traceability", is only on the verge of being solved.

The rest of this paper will be devoted to how to obtain traceability in the determination of the calorific value of natural gas and thereby the traceability of the analysis of gas by gas chromatography.

3.0 Working towards traceability in the analysis of natural gas.

Looking again at table 1: The different parameters that are necessary for obtaining an accurate analysis of gas, it can be said that within ISO TC 193 SC1[1] there is being done a lot of work to cope with the first three of the parameters, ref. (5) and ref. (6). The training of the operator is then mainly a point of she/he regularly operating the chromatograph following the accepted standards.

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[1] ISO TC 193 SC1: International Standards Organization: Technical committee 193 on Natural Gas; Subcommittee 1 on Natural Gas Analysis.

Therefore the remaining problem of obtaining traceability in gas analysis is the traceability of the reference gas mixtures applied to calibrate or check the analysis equipment.

3.1 Reference gas mixture.

A reference gas mixture is a mixture of pure gases that often closely resembles the natural gas to be measured upon. The mixture is usually prepared using gravimetrical techniques which still is the most accurate method of preparing gas mixtures.

ISO Standard 6142 (ref. 7) gives guidelines in the preparation of these reference gas mixtures. But the standard is too general a standard to achieve reproduceability between different laboratories. Fortunately actions are being taken now to revise this standard also in the forum of ISO TC 193 SC1.

The uncertainty of the composition of the reference gas mixture is of great importance as the uncertainty of the determination of the molar composition of the gas sample is directly proportional to the uncertainty of the reference gas mixtures.

In table 3 is seen some of the major parameters in preparing reference gas mixtures that can contribute to the uncertainty of the mixture. As can be seen several parameters contribute to the uncertainty of the reference gas mixture besides the weighing procedure.

Table 3 Some major parameters in gas mixing

1.	Impurities of the gases used in the mixing.
2.	Lack of knowledge of impurities.
3.	Lack of cleanlines of the gas cylinders, and the mixing system(e.g. valves,tubing)
4.	Insufficent filling/weighing procedures.

After having mixed the gas the question of checking the gas mixtures arises and the methods of checking or analysing the reference gas mixture are often less accurate than the methods of preparing the gas mixture (gas chromatography versus gravimetrical techniques).

Following up on the preparation of the reference gas mixture parameters that are often forgotten are the stability of the mixture and the influence of the different pressures of the gas as the reference gas mixture is being used.

3.2 Traceability of reference gas mixtures.

The interest in traceability in analysis of gas in general and thereby in reference gas mixtures is reflected by the number of European and International groups that are working towards obtaining traceable determinations. In table 4 some of the groups are mentioned.

Table 4

Organization	Working Groups
1. WECC[2]	Reference Materials.
2. ISO TC 193 SC1	Traceability in natural gas analysis.
3. ISO-REMCO[3]	Reference Materials.
4. EURACHEM[4]	No 5: Calibration in Chemistry.

All the groups mentioned have as one of their work items promised to obtain a close liason with other relevant working groups to avoid double work. And in fact at least one person: Deputy Manager mr. Anton Alink of the VSL of NMi[5], is a member of all four working groups. FORCE-Dantest has a close contact through NMi to the work and is a member of the first 2 working groups. FORCE-Dantest is representing the Danish Institute for Fundamental Metrology in the WECC working group. All of these working groups are no more than 2 years old.

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[2] WECC: Western European Calibration Cooperation

[3] ISO-REMCO: Council Commitee on Reference Materials

[4] EURACHEM: European Analytical Chemistry in General

[5] VSL of NMi: The Van Swinden Laboratorium of The Netherlands Measurements Institute, Holland

In the following will be given a short description of the scopes of the two first mentioned working groups and a status of the work in the groups up to now.

3.2.1 WECC:

As a working group for a cooperation of calibration services the main scope of this working group is to develop guidelines (protocols) that the calibration services of each country can use to accredit laboratories. In this case the laboratories are gas manufacturers who manufacture reference gas mixtures.

The initial protocols are at this state being set up by members of NMi, BNM, NPL and SFM[6]. In Europe there exists three manufacturers of gas that are already accredited following national protocols and for reference gas mixtures that are relevant for the measurement of exhaust gases. They are situated in Switzerland. In England and Holland several gas manufacturers have shown an interest in accreditation.

Another important purpose is to establish a close cooperation between the different countries in establishing reference gas mixtures with the level of primary gas standards. These can be produced by the National Standards Laboratory or by equivalent laboratories i.e. laboratories which are authorized by each government. One of the major aspects of this is the necessary intercomparisons between these laboratories and exchange of information. Laboratories that at this stage manufacture primary gas standards are NMi, NPL and NIST[7].

The major result of this work is to obtain the possibility that traceability of a reference gas mixture can be obtained through comparison to primary gas standards.

3.2.2 ISO TC 193 SC1 Advisory group: Traceability.

The main aim of this group is to aid the working groups of the SC1 in obtaining the description of traceable methods in their standards. The advisory group therefore set up a scope in which primarily general guidelines should be made by the group which the other working groups should apply to their standards.

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[6] NMi: Netherlands Measurements Institute, Holland
BNM: Bureau National de Metrologie, France
NPL: National Physical Laboratory, UK
SFM: The Swiss Federal Office of Metrology, Switzerland

[7] NIST: National Institute of Standards and Technology, USA

Secondarily the advisory group would then review each draft standard for the correctness of the application of the guidelines. The guidelines were given out as a 1 st. draft in June 91 and were also submitted to ISO-REMCO (Ref. 1).

Although the guidelines are far from finished they give an idea in what direction the advisory group is aiming namely again that traceability of a reference gas mixture can be obtained through comparison to primary gas standards.

The guidelines are meant for ISO standardization groups who have to implement traceability in their standards but the guidelines can be used in many other connections although not at the level of the natural gas analytical equipment.

3.3 Summarizing

- The traceability in measurement of natural gas quality corresponds in this paper to the traceability in analysis of natural gas using gas chromatography.

- One of the major problems in obtaining traceability in the analysis of natural gas using gas chromatography is the lack of traceability of the reference gas mixtures used to calibrate or check the gas chromatographs.

- Several International and European working groups are working on solving the problems for nearly all levels in the traceability chain of reference gas mixtures. And the major idea is that traceability of a reference gas mixture can be obtained through comparison to primary gas standards.

4.0 Conclusions

Each level in the traceability chain of reference gas mixtures is being worked on except possibly the level of the natural gas analytical equipment. The major idea being that traceability of a reference gas mixture can be obtained through comparison to primary gas standards.

The Norwegian Petroleum Directorate has asked FORCE-Dantest to produce guidelines for traceability in measurement of natural gas quality, (ref. 2) that could be used at the level of the analytical equipment. A first draft of the guidelines has been completed and comments to these guidelines and how to implement them are very welcome.

To help the work being done it is now necessary for us, the users, to begin possibly not yet demanding that, but at least enquiring whether our gas manufacturers follow this work as closly as possible.

One thing is to establish guidelines another is to put them to use, here is where all of us can be of help. Even at this early stage the awareness of the necessity and possibility of traceability will help the cause.

The possibility of obtaining traceable reference gas mixtures following the concepts described in this paper is not possible at this stage except from a few National Standards Laboratories of which the larger are NIST, NMi and NPL.

But in 5 years time we will hopefully be looking back and saying: Traceability in measurement of natural gas quality - No problem!

5.0 Postscript

One of the major problems in the methods for checking reference gas mixtures is that the accuracy level of the methods are often many times less than the preparation methods of the gas mixtures. At the Gas Density Laboratory at FORCE-Dantest we have a method for checking reference gas mixtures. It will not check the mole fraction of each constituent but will check the overall uncertainty and thereby detect any major error sources. The uncertainty of this method is very close to the uncertainty of the preparation method. The method is based on the determination of the mole mass of gas and a project partially funded by the National Council of Metrology in Denmark has been performed to prove the efficiency of this method, ref. (8).

6.0 Reference list

1) ISO TC 193 SC1. Advisory Group Traceability: General Features of traceability in the analysis of gas.

2) FORCE-Dantest: Guidelines for traceability in measurement of natural gas quality, 1990-04-26

3) ISO 6976: Natural Gas - calculation of Calorific Values, Density, Relative Density and Wobbe Index from Composition.

4) BIPM/IEC/ISO/OIML/IFCC/IUPAC:
International vocabulary of basic and general terms in metrology (VIM). Draft revision 1989.

5) ISO/DIS 10723:
Natural gas-analysis of natural gas and natural gas substitutes - performance evaluation.
(DIS: Draft International standard)

6) ISO 6974 - Natural Gas - Determination of hydrogen, inert gases and hydrocarbons up to C8 - Gas chromatographic method.

This document is now being revised by ISO/TC 193 SC1 WG8: Natural gas - The determination of natural gas composition for the calculation of calorific value, density and wobbe-index with calculable uncertainty. Gaschromatographic method.(Working Group Draft)

7) ISO 6142 Gas Analysis - Preparation of calibration gas mixtures - Weighing Method.

8) The FORCE Institutes: Determining the Mole Mass of Gas-Verification of a method that can be used in quality control of reference gas mixtures.