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FEASIBILITY STUDY OF A CORRELATIVE ENERGY MEASUREMENT SYSTEM FOR NATURAL GASES

P. Schley[1], R. Kleinrahm[2], M. Jaeschke[1], R. Janssen-van Rosmalen[3] and J.A. Schouten[4]

[1] Ruhrgas AG, Halterner Strasse 125, 46284 Dorsten, Germany
[2] Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum, 44780 Bochum, Germany
[3] N. V. Nederlandse Gasunie, P.O. Box 19, 9700 MA Groningen, the Netherlands
[4] Johann Buyeslaan 24, 1141 GT Monnickendam, the Netherlands

Abstract: The paper presents a new correlative energy measurement method developed under a joint project of Ruhrgas AG, Germany, and Nederlandse Gasunie N. V., the Netherlands. The paper mainly refers to the results obtained from a previous feasibility study proposing a method using as input parameters dielectric permittivity, speed of sound and CO_2 *mole fraction. On the basis of these input parameters, superior calorific value and natural gas composition can be determined. Total uncertainty envisaged for superior calorific value is 0.2 %. Initial laboratory tests confirm that the uncertainty envisaged can be obtained or is even better. The method is to be tested in the field soon.*

Keywords: Calorific Value, Dielectric Permittivity, Energy, Natural Gas, Speed of Sound

1 INTRODUCTION

For custody transfer metering of natural gas, energy flow must be known very accurately. Energy flow is the product of superior calorific value multiplied by volume flow at normal conditions. Superior calorific value is usually measured with a combustion calorimeter or obtained from gas composition determined by a process gas chromatograph (PGC). Volume flow is measured with orifice plates or turbine meters, recently also with ultrasonic flowmeters. Volume must then be converted from volume at flowing conditions to volume at normal conditions. This is usually done using an equation of state, such as the SGERG equation [1,2]. The SGERG equation requires as input data superior calorific value, normal density and CO_2 mole fraction. If superior calorific value is determined using a calorimeter, additional measurements must be made to determine density at normal conditions and CO_2 mole fraction. If a PGC is used, gas composition will provide the input data required for the SGERG equation. As an alternative to the SGERG equation, conversion is also possible by measuring density at flowing conditions and density at normal conditions.

In 1998, Ruhrgas AG, Germany, and Nederlandse Gasunie N. V., the Netherlands, started a joint project to examine future energy measurement. The project aims to develop a new energy measurement method which, in addition to conventional flow measurement, uses physical input properties from which both superior calorific value and volume conversion factor can be derived. The new method is expected to involve lower capital outlay and maintenance costs than current energy measurement methods on the basis of calorimeters or PGCs. Total uncertainty envisaged for superior calorific value is 0.2 %.

In preparation for the project, two studies were ordered to have such a correlative method examined for its feasibility. The studies were made by Ruhrgas and Ruhr-Universität Bochum and by van der Waals-Zeemann Laboratory which was retained by Gasunie.

2 SELECTION OF PHYSICAL PROPERTIES

At least three physical properties are required to characterize the composition and superior calorific value of natural gases. More details on this statement are given in Section 3. The following physical properties, among others, were examined in connection with correlative energy measurement: superior calorific value, density, speed of sound, dielectric permittivity, viscosity, thermal conductivity, isobaric heat capacity, CO_2 mole fraction. The criteria to assess suitability of the various input properties included the following:

a) Low experimental measurement uncertainty.
b) High sensitivity of the parameters with respect to gas composition - in particular with respect to the main components CH_4, C_2H_6, N_2, CO_2.
c) Input properties not to correlate with each other.
d) Low capital outlay and maintenance costs.

Basically, criteria a) to c) determine total uncertainty of the superior calorific values derived. To simplify matters, a three-component mixture is used to determine in a first step the input property combinations basically suitable for energy determination and the superior calorific value uncertainties involved. As an example, we use a mixture consisting of methane, ethane and nitrogen, the three main natural gas components. A good description of the mixture by two input properties is a precondition for a natural gas to be also characterized in a sufficient accurate manner in combination with a third input property (CO_2 mole fraction could, for example, be used as a third parameter; it can easily be measured in natural gases using infrared absorption).

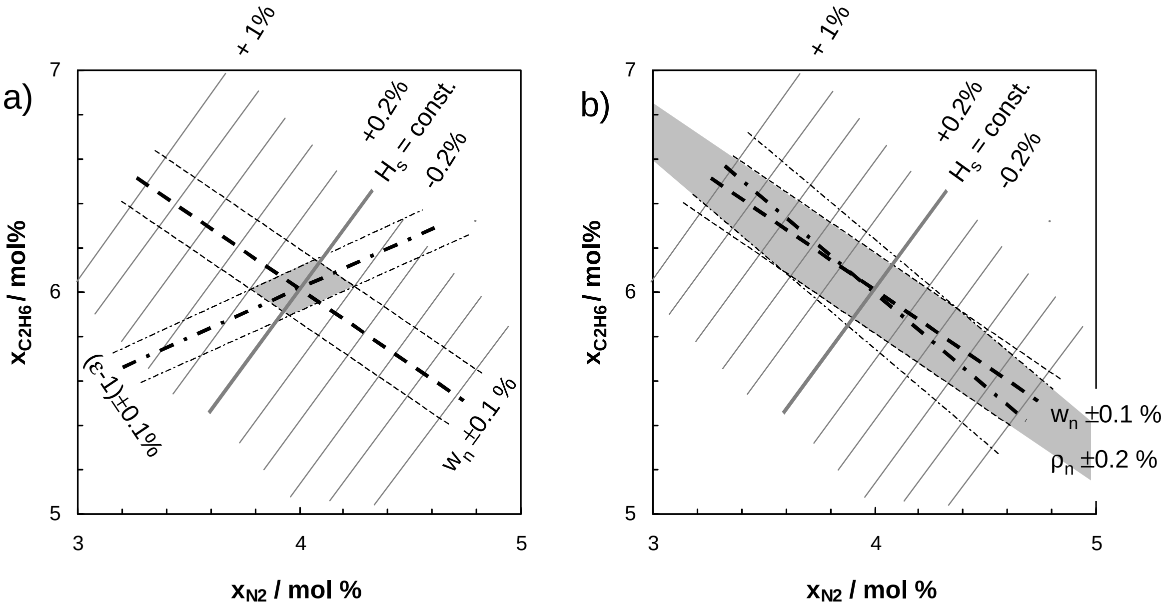

Fig. 1: Superior calorific value determination for CH_4+C_2H_6+N_2 mixture using two input properties
a) Suitable combination b) Unsuitable combination

Figs. 1a) and 1b) show two different input property combinations: Fig. 1a) is based on speed of sound $w(p_n,T_n)$ (T_n = 273.15K, p_n = 0.101325 MPa) and dielectric permittivity ε(1 MPa, 293.15 K), Fig. 1b) on speed of sound $w(p_n,T_n)$ and density (p_n,T_n). The first combination produces good results with respect to superior calorific value while the results obtained from the second combination are not satisfactory.

The graphs plot ethane mole fraction against nitrogen mole fraction. Methane mole fraction corresponds to the difference x_{CH4} = 100 - x_{C2H6} - x_{N2}. We use as an example a mixture consisting of x_{CH4} = 90 mol %, x_{C2H6} = 6 mol % and x_{N2} = 4 mol %. Each graph shows the isolines through the reference point so determined for both superior calorific value and the respective input parameters. Further superior calorific value isolines are included for ±0.2 %, ±0.4 %, ±0.6 %, ±0.8 % and ±1 %

referred to the reference point. Also, the experimental measurement uncertainties assumed for the respective input parameters are limited by two isolines for each parameter. Total superior calorific value uncertainty resulting from experimental uncertainty corresponds to the intersection area of the two uncertainty margins shown for the respective input parameters (shaded area). Total superior calorific value uncertainty associated with the first combination in Fig. 1a) is approx. 0.2 % for the assumed experimental uncertainties of Δw_n = 0.1 % for speed of sound and $\Delta(\varepsilon\text{-}1)$ = 0.1 % for dielectric permittivity. Superior calorific value uncertainty for the second combination exceeds 2 % (Fig. 1b, Δw_n = 0.1 % and $\Delta\rho_n$ = 0.2 %). The graph shows almost parallel curves for the input parameters used in this combination. This means the parameters are highly correlated with each other.

The approach described is a good means to exclude from the great number of possible combinations those which are obviously not suitable for use in energy measurement (such as the combination shown in Fig 1.b). We isolated the combinations which seemed suitable and used the correlation method presented in Section 3 to calculate for natural gases superior calorific value sensitivity to the respective input parameters and total uncertainty involved. With this approach, we examined a large number of possible combinations. On the basis of the assessment criteria mentioned above, we found the following three input parameters the most favourable combination: speed of sound, dielectric permittivity and CO_2 mole fraction [3].

Speed of sound and dielectric permittivity can usually be measured at flowing conditions (p, T) or at specific reference conditions. In the case of dielectric permittivity, however, measurement accuracy deteriorates as pressure decreases so that a minimum pressure of $p \approx 1$ MPa is probably required. As an alternative to speed of sound, density could be used. Superior calorific value uncertainties are similar for both parameters. But speed of sound is probably the more cost-effective alternative.

3 CORRELATION METHOD FOR NATURAL GASES

This correlation method is based on the assumption that natural gas can be characterized in a sufficiently accurate manner as a three-component mixture consisting of

- nitrogen N_2,
- carbon dioxide CO_2,
- equivalent hydrocarbon gas CH.

This relation was already used for the SGERG equation [1,2]. The hydrocarbon gas designated CH in the following mainly consists of n-alkanes. The n-alkane mole fractions in natural gases are subject to regular distribution and can therefore be clearly characterised by a single parameter.

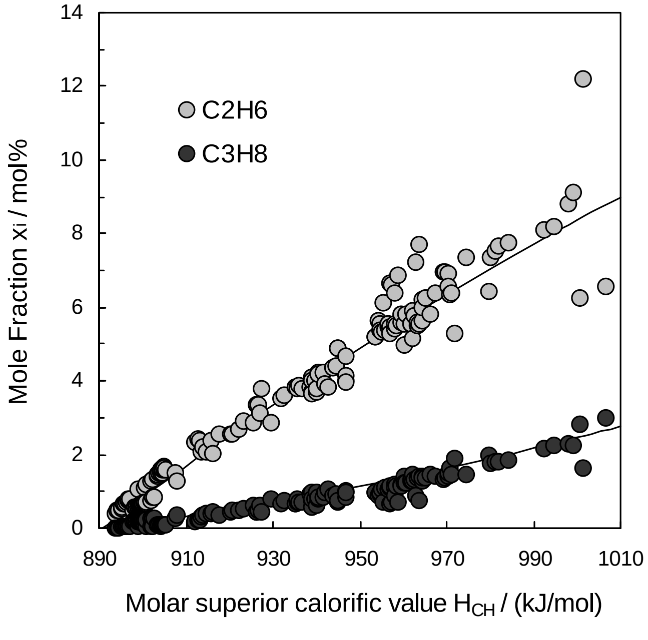

Fig. 2: Ethane and propane mole fractions as a function of molar superior calorific value H_{CH} for 210 natural gas samples

Fig. 2 is a graphic representation showing ethane and propane mole fractions as a function of the molar superior calorific value H_{CH} of the pure hydrocarbon gas for various natural gases. The result shown includes 210 GC analyses covering the entire range of typical europeen natural gases. The graph was prepared by reducing natural gas composition to pure hydrocarbon gas by setting the inert gas fractions, mainly nitrogen and carbon dioxide, to equal zero. We then normalized the natural gas analysis to 100 mol % and calculated molar calorific value H_{CH} from the reduced composition in accordance with ISO 6976.

As Fig. 2 shows for ethane and propane, alkane mole fractions can be formulated as simple functions of superior calorific value H_{CH}. Equation (1) was correlated for a total of nine alkanes (C_2H_6, C_3H_8, n-C_4H_{10}, i-C_4H_{10}, n-C_5H_{12}, i-C_5H_{12}, n-C_6H_{14}, n-C_7H_{16}, n-C_8H_{18}).

$$x_{CH,i} = \left(a_{1,i} \cdot (H_{CH} - 890.63\,\mathrm{kJ/mol}) + a_{2,i} \cdot (H_{CH} - 890.63\,\mathrm{kJ/mol})^2\right) \cdot x_{CH} \qquad (1)$$

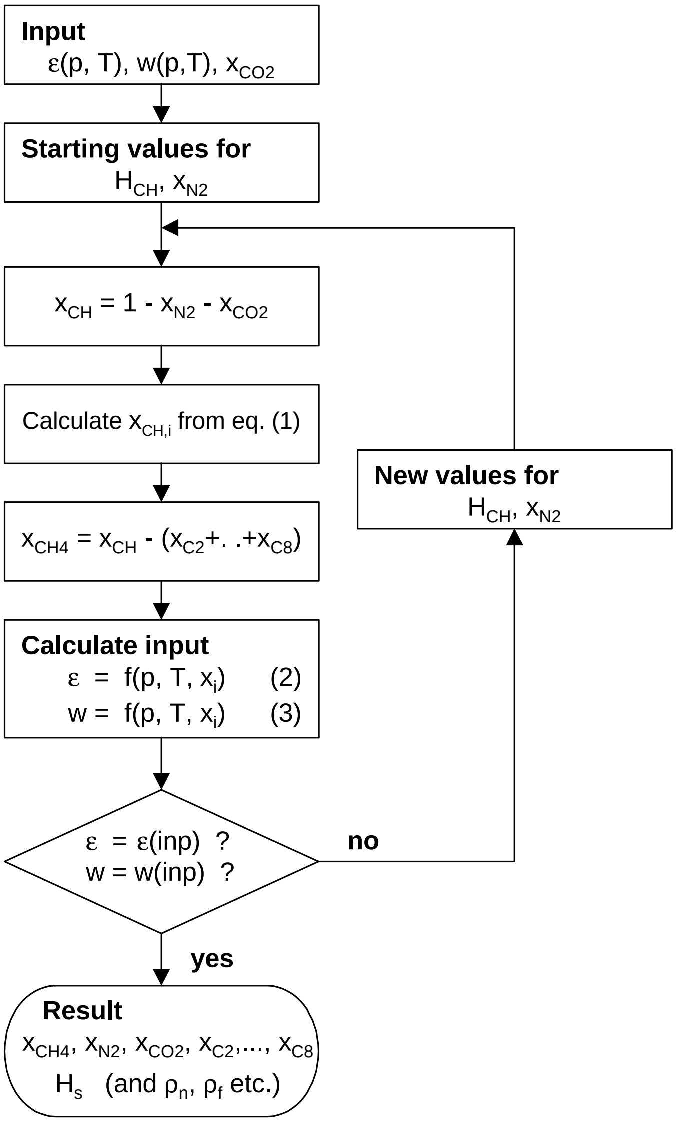

Fig. 3: Procedure to calculate gas composition and superior calorific value from dielectric permittivity, speed of sound and CO_2 mole fraction

An iterative method was developed on the basis of this equation which allows to determine superior calorific value and gas composition of a twelve-component mixture using three input parameters [4]. From the gas composition additional properties such as density at normal and flowing conditions (ρ_n, ρ_f) required for volume conversion can be derived. Fig. 3 shows the iterative procedure using as an example speed of sound, dielectric permittivity and CO_2 mole fraction as input properties. In addition to the input properties, the p, T reference conditions for speed of sound w and dielectric permittivity ε must be known. Also, the iterative method requires formulation of w and ε as a function of p, T and x_i (equations (2) and (3) in Fig. 3). It is a focal point of the project to develop and verify these equations in extensive laboratory tests.

The calculation procedure was tested on the 210 gas samples also treated in Fig. 2. The input properties speed of sound dielectric permittivity and CO_2 mole fraction were derived from gas analysis. Fig. 4 shows the relative deviations of superior calorific values determined with the correlation method from values derived from GC analysis. The maximum deviations are below 0.04 %; they result from purely systematic correlation errors and do not contain any experimental uncertainties.

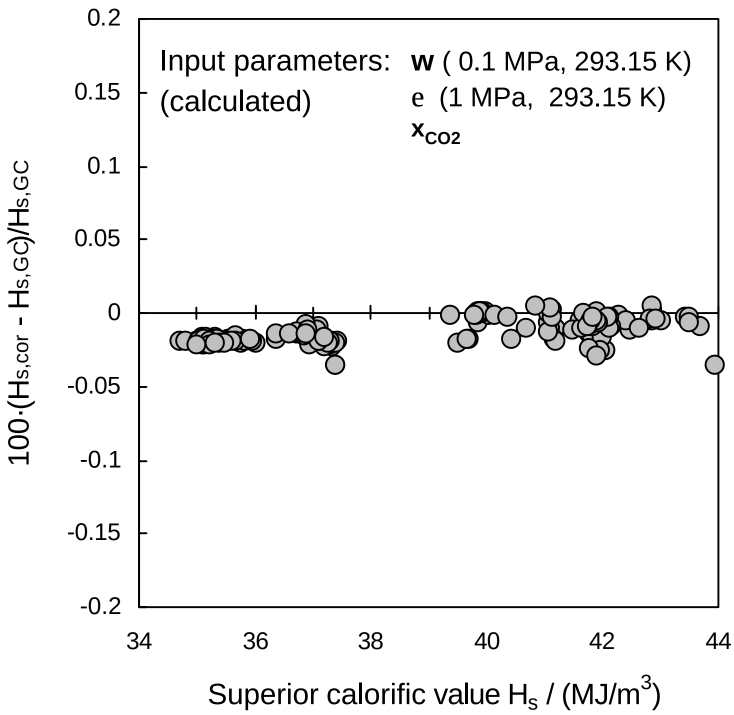

Fig. 4: Deviations of superior calorific values determined with the correlation method from values derived from GC analysis for 210 gas samples. The input parameters w, ε and x_{CO2} were calculated from GC analysis.

4 MEASUREMENT METHODS FOR INDIVIDUAL COMPONENTS

To obtain the total uncertainty of 0.2 % envisaged for superior calorific value, the following input parameter uncertainties must be observed:

- Speed of sound Δw = 0.1 %
- Dielectric permittivity $\Delta(\varepsilon\text{-}1)$ = 0.1 %
- CO_2 mole fraction Δx_{CO2} = 0.3 mol %

For both speed of sound and dielectric permittivity, there are various measurement methods which have proven successful at laboratory level but have not yet been implemented in a field instrument. This project therefore examined several methods for their suitability in the measurement of these two properties and provided laboratory set-ups for some of them. The laboratory measurement methods were designed to reflect as best possible future field instrument requirements. With respect to CO_2 mole fraction measurement, there are satisfactory field instruments available operating on the basis of infrared absorption and providing the accuracies required.

4.1 Speed of Sound

Speed of sound can be determined by time of flight measurement using an ultrasonic flowmeter. Both a 4" ultrasonic flowmeter and a conventional domestic ultrasonic flowmeter were used. In case of the domestic meter the speed of sound is determined at atmospheric pressure. The tests confirmed for both cases better results than the total uncertainty of 0.1 % envisaged. Of course, the domestic meter is available at a significantly lower price.

4.2 Dielectric Permittivity

Two different concepts were pursued for dielectric permittivity. The National Engineering Laboratory (NEL), Glasgow, UK, developed an LC resonator (L: inductance, C: capacitance) on the basis of the method published by Goodwin [5]. The measurement cell shown in Fig. 5 is excited at approx. 400 MHz. Dielectric permittivity can be derived directly from resonance frequency. Laboratory tests confirmed clearly better results than the experimental uncertainty specified of 0.1 % referred to (ε-1).

At the same time, the van der Waals-Zeemann Laboratory was retained to develop a concentric cylinder capacitor. The dielectric permittivity can be assessed directly from the measured capacity. This conventional measurement method, described in [6] for example, operates at 40 kHz. First laboratory tests are expected soon.

Fig. 5: LC resonator measurement cell

5 LABORATORY MEASUREMENTS

5.1 Measurements on Pure Gases and Binary Mixtures

As already mentioned, a focal point of the project is to select and/or identify suitable equations formulating the input parameters used as a function of pressure, temperature and gas composition. These equations are required for the iterative correlation procedure in Section 3. The AGA8 equation [7] is a suitable equation of state for speed of sound. It was already extensively tested under the GERG project [8]. For dielectric permittivity, the Clausius Mossotti function can be used to establish a correlation with molar density in the form of a virial equation:

$$CM = \frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{1}{\rho_m} = A_\varepsilon + B_\varepsilon \cdot \rho_m + C_\varepsilon \cdot \rho_m^2 \qquad (4)$$

The AGA8 equation [7] can be used to calculate molar density as a function of p, T, and x_i. The dielectric virial coefficients A_ε, B_ε and C_ε of a gas mixture, for example of a natural gas, can be determined from the dielectric virial coefficients of the pure gases using simple mixture rules.

Laboratory measurements with the NEL resonator therefore first focused on the dielectric virial coefficients of pure gases as these are usually not known from literature in a sufficiently accurate manner. In this connection, measurements were made on methane and nitrogen as pure gases and on a total of 20 binary mixtures at pressures of up to 10 MPa. The binary mixtures each consisted of methane and another natural gas component with varying mole fractions. The binary mixture measurements served to determine the dielectric virial coefficients of the alkanes ethane to hexane on the one hand and to identify a suitable mixing rules on the other.

5.2 Measurements on Natural Gases

To test the new energy measurement system, simultaneous measurements of dielectric permittivity, speed of sound and CO_2 mole fraction were performed for 10 natural gases. The dielectric permittivity was measured with the NEL resonator at approx. 1 MPa. The speed of sound was determined with a domestic ultrasonic flowmeter at atmospheric pressure. For the carbon dioxide mole fraction measurement a conventional CO_2-Sensor based on infrared absorption was used. From these input parameters superior calorifc values were determined and compared with values derived from GC-analysis. The relative deviations given in Fig. 6 are less than 0.05 % in all cases.

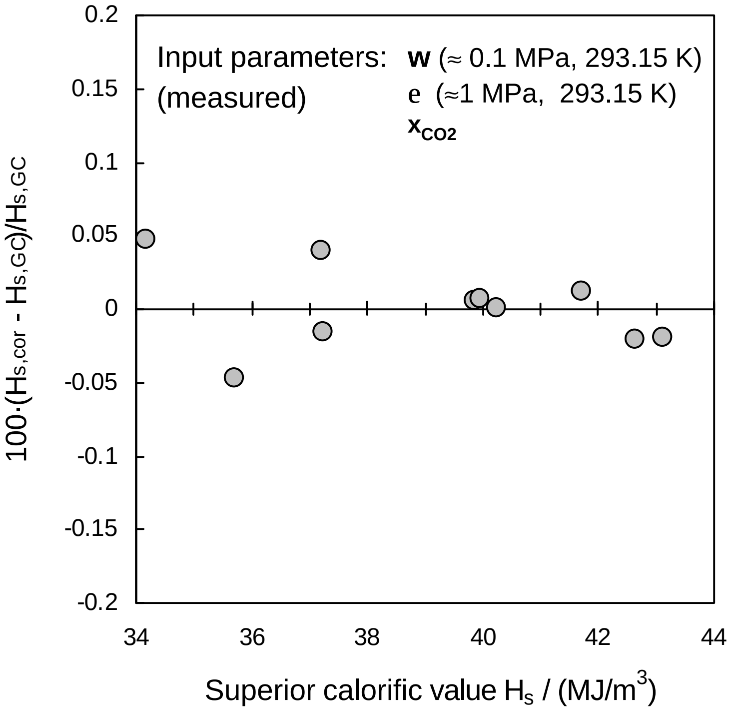

Fig. 6: Deviations of superior calorific values determined with the correlation method from values derived from GC analysis.

Measured values for density at normal condition and CO_2 mole fraction, needed as input parameters for conversion factor determination according to the SGERG-equation [1,2], are also in excellent agreement with values obtained from GC-analysis. Initial field testing of the measurement method is scheduled for mid-2000.

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AUTHORS:

1 Ruhrgas AG, Energy Measurement, Instrumentation & Control, Simulation, Halterner Strasse 125, 46284 Dorsten, Germany. E-mail: peter.schley@ruhrgas.com; manfred.jaeschke@ruhrgas.com

2 Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum, 44780 Bochum, Germany.
E-mail: Kleinrahm@thermo.ruhr-uni-bochum.de

3 N. V. Nederlandse Gasunie, R&D Gas Measurement, P.O. Box 19, 9700 MA Groningen, the Netherlands. E-mail: R.Janssen.van.Rosmalen@gasunie.nl

4 Johann Buyeslaan 24, 1141 GT Monnickendam, the Netherlands. E-mail: Schouten@wins.uva.nl