TEXTE

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Validation and quality assurance of methods for the substance flow analysis for large carbon dioxide loads from CO_2 separation in CCS power stations

For our Environment

Umwelt Bundesamt

TEXTE 52/2015

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Validation and quality assurance of methods for the substance flow analysis for large carbon dioxide loads from CO_2 separation in CCS power stations

by

Bernhard Hoff, Hans Schmidt
TÜV/SÜD Industrie Service GmbH, Filderstadt, Germany

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Publisher:
Umweltbundesamt
Wörlitzer Platz 1
06844 Dessau-Roßlau
Tel: +49 340-2103-0
Fax: +49 340-2103-2285
info@umweltbundesamt.de
Internet: www.umweltbundesamt.de

/umweltbundesamt.de
/umweltbundesamt

Study performed by:
TÜV/SÜD Industrie Service GmbH
Umwelt Service
Gottlieb-Daimler-Str. 7
70794 Filderstadt
Germany

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Section E 2.1 DEHSt Deutsche Emissionshandelsstelle
Vanessa Wagner

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Abstract

This report describes the specification of a suitable measurement system for the qualitative and quantitative assessment of fluids with a high carbon dioxide content, as is typical for CCS systems.

- Checking of the technical prerequisites of various pilot and test rigs for CO_2 separation and of industrial plant on which measurements systems for the quantitative measurement of CO_2 flows already in existence could be tested. The focus of the review is the determination of existing boundary conditions as well as the measurement systems technologies installed in plants.
- Development and performance of a test- programme for CO_2 flow measurement-systems at a test facility (gas flow calibration loop)
- Assessment of the contributions to the uncertainty of the measurement results from the tests, based on the suitability test procedure prescribed for the approval of continuous measurement equipment and the achievable total measurement uncertainty with regard to the Monitoring Monitoring and Reporting Regulation (MRR).
- Recommendations for the use of continuous flow measurement equipment for the monitoring of CCS gases (and for the use in industrial plant for the purpose of CO_2 monitoring in accordance with the MRR) were to be given on the basis of this investigation.

Summary of results:

The use of continuous CO_2 measurement equipment in industrial plant is possible. The measurement method used works reliably with the established quality assurance measures. Compliance with the highest tier in accordance with the Monitoring and Reporting Regulations is not possible. The uncertainty must be determined individually for the respective measurement equipment and optimised, if applicable.

There are no test results for flow meters which can be used with compressed waste gas. By comparison with the measurement methods used for atmospheric measurements, a large error contribution is to be expected due to this. Further investigations and development by equipment manufacturers are required.

Kurzbeschreibung

Der Bericht beschreibt die Festlegung eines geeigneten Messsystems zur qualitativen und quantitativen Bewertung von Fluiden mit hohen Kohlendioxidgehalten, wie sie für CCS-Systeme typisch sind. Die Vorgehensweise gliederte sich in folgende Einzelschritte:

- Prüfung der technischen Voraussetzungen verschiedener Pilot-und Versuchsanlagen zur CO_2-Abscheidung sowie Industrieanlagen, an denen bereits vorhandene Messsysteme zur quantitativen Erfassung von CO_2-Strömen getestet werden können.
- Erarbeitung und Durchführung eines Test- Programmes für CO_2-Durchflussmess-systeme an einer Versuchsanlage.
- Auswertung der Beiträge zur Unsicherheit von Messergebnissen in Bezug auf das für die Zulassung von kontinuierlichen Messeinrichtungen vorgeschriebene Eignungsprüfungsverfahren und Abschätzung der erreichbaren Gesamtmessunsicherheit im Hinblick auf die Monitoringverordnung (MVO).
- Empfehlungen für den Einsatz von kontinuierlichen Durchflussmesssystemen bei der Überwachung von CCS-Abgasen (und auch im Einsatz an Industrieanlagen zum Zweck der CO_2-Überwachung nach MVO)

Zusammenfassung der Ergebnisse:

Der Einsatz von kontinuierlichen CO_2-Messeinrichtungen bei Industrieanlagen ist möglich. Die einsetzbare Messtechnik arbeitet zuverlässig mit eingeführten Verfahren zur Qualitätssicherung. Die Einhaltung der höchsten Ebene nach Monitoringverordnung ist nicht möglich. Die Messunsicherheit muss individuell für die Messeinrichtung ermittelt und gegebenenfalls optimiert werden.

Es liegen keine Prüfergebnisse von Durchflussmessgeräten vor, die im komprimierten Abgas eingesetzt werden können. Durch Vergleich von eingesetzten Messverfahren bei atmosphärischen Messungen wird hierdurch ein großer Fehlerbeitrag erwartet. Es besteht Untersuchungsbedarf und Weiterentwicklungsbedarf für die Gerätehersteller.

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Abbreviations

AMS	Automatic Measurement System
AST	Annual Surveillance Test
BEPÜ	Uniform Nationwide Practice for Monitoring Emissions
CEMS	Continuous Emission Monitoring System
CFD	Computational Fluid Dynamics
EIP	Suitability Test
ELV	Emission Limit Value
MVO, en: MRR	Monitoring and Reporting Regulation
QAL1	1. Quality Assurance Stage as per DIN EN 14181 (Suitability Test)
QAL2	2. Quality Assurance Stage as per DIN EN 14181 (Calibration)
QAL3	3. Quality Assurance Stage as per DIN EN 14181 (Ongoing quality assurance at operator)
Rfield	Reproducibility
s	Standard Deviation
σ	(Total) Error
SRM	Standard Reference Measurement Procedure
StdMW	Hourly Average Value
TMW	Daily Average Value
uc	Total Uncertainty
USD	Ultrasound Flowmeter

1 Summary

The aim is to specify a suitable measurement system for the qualitative and quantitative assessment of fluids with a high carbon dioxide content, as is typical for CCS systems, based on the measurement procedures and measurement methods named by the Client. A suitable test location was to be selected in consultation with the Client to test the measurement system in initial tests with regard to its suitability.

To date, many of the methods and procedures/techniques to be considered have not yet been tried and tested nor have they been trialled nor proven. The regulatory authorities are aware that the knowledge is currently not completely available for the reliable assessment of a CCS programme.

At the start of the project, it was not possible to specify suitable measurement systems and measurement methods. No additional moneys were available to equip potential test locations with appropriate measurement equipment. Thus, the aim was extended to the following preparatory steps:

- Checking of the technical prerequisites of various pilot and test rigs for CO_2 separation and of industrial plant on which measurements systems for the quantitative measurement of CO_2 flows already in existence could be tested. The focus of the review is the determination of existing boundary conditions as well as the measurement systems technologies installed in plants.
- Contacting manufacturers of measurement equipment with the objective of obtaining measurement equipment free of charge to supplement the existing measurement systems in the above test installations. The actual experience of the manufactures with CCS measurement conditions was to be summarised.
- Contact with TÜV SÜD NEL in Glasgow (UK) regarding the examination of possibilities of carrying out tests (CO_2 flow and CO_2 concentration measurements) on their test facility.
- On-site meeting with TÜV SÜD NEL and drawing up of a test programme together with the Client (UBA).
- Subcontracting TÜV SÜD NEL with carrying out test programmes for CO_2 flow and CO_2 concentration measurements on their test facility.

The major steps of the project are listed below in chronological order:

- 08.11.2011: Contact with Stuttgart University, Department of Combustion and Power Plant Technology (IFK), regarding the possibility of carrying out laboratory tests (CO_2 concentration measurements) in their research laboratory.

  Note: The work with Stuttgart University (IFK) is not the subject of this UFOPLAN research and development project. It is dealt with under the experts' opinion FKZ 390 01 025:

  "Evaluation of Measurement Equipment for the Quantification of Carbon Dioxide in Typical Waste Gases from Industrial Plant, Power Industry and Fuel Preparation Installations"
- 09.04.2012: Contact with TÜV SÜD NEL in Glasgow (UK) regarding the examination of possibilities of carrying out tests (CO_2 flow and CO_2 concentration measurements) on their test facility.
- 25.05.2012: Submission of the first interim report (Progress Report 05/12) to the Federal Environment Agency.
- 15.06.2012 On-site meeting at TÜV SÜD NEL in Glasgow:
  During this meeting, a test programme for CO_2 flow and CO_2 concentration measurements was drawn up together with the Client (UBA) and TÜV SÜD NEL was

commissioned with the implementation of this test programme, which was divided into 2 work packages (WP1+2).

WP1: Examination of flow measurement systems for CO_2 flows

WP2: Examination of concentration measurement systems for CO_2

The tests of the flow measurement systems on the TÜV SÜD NEL test facility (gas flow calibration loop) were to be carried out as comparisons as there is currently no primary standard for flow measurement of liquid or gaseous CO_2.
The contributions to the uncertainty of the measurement results from the tests were to be assessed based on the suitability test procedure prescribed for the approval of continuous measurement equipment and the achievable total measurement uncertainty was to be assessed with regard to the MRR.
Recommendations for the use of continuous flow measurement equipment for the monitoring of CCS gases (and for the use in industrial plant for the purpose of CO_2 monitoring in accordance with the MRR) were to be given on the basis of this investigation.

Note: Work Package 1 was carried out in October 2012 on the TÜV SÜD NEL test rig, Work Package 2 was to be carried out in January/February 2013, also on the TÜV SÜD NEL test rig. Due to technical problems, this work package could not be carried out during the period intended. As completion of the project in June 2013 was given priority by the Client, this part of the investigation could not be carried out.

- 18.09.2012: The first results of the flow measurement testing programme started by TÜV SÜD NEL and how to proceed further were discussed during a coordination meeting at the Federal Environment Agency.
- 16.11.2012: Submission of the second interim report (Progress Report 11/12) to the Federal Environment Agency.
- 05.06.2013: Submission of the final report (draft) during a workshop at the Federal Environment Agency.

The continuous emissions measurement of air pollutants in industrial waste gases has become operational practice following the introduction of air pollution control and the emissions monitoring regulations. CO_2 is no air pollutant and thus not a waste gas component subject to monitoring. The operator can use measurement equipment tested for suitability.

The use of continuous CO_2 measurement equipment in industrial plant is possible. The measurement method used works reliably with the established quality assurance measures. Compliance with the highest tier in accordance with the Monitoring and Reporting Regulations is not possible. The uncertainty must be determined individually for the respective measurement equipment and optimised, if applicable.

There are no test results for flow meters which can be used with compressed waste gas. By comparison with the measurement methods used for atmospheric measurements, a large error contribution is to be expected due to this. Further investigations and development by equipment manufacturers are required, in particular due to standard EN 16911-2 [11] which has come into force in June 2013.

Based on the results obtained, the uncertainty due to calibration provides a small contribution to the total uncertainty.It appears to be possible to measure the concentration of compressed, highly concentrated CCS gas with a relatively low uncertainty. Gas sampling and relaxation to atmospheric conditions have not been investigated. There is currently no application in Germany, and we do not know of any outside Germany.

2 Zusammenfassung

Gemäß Aufgabenstellung sollte ein geeignetes Messsystem zur qualitativen und quantitativen Bewertung von Fluiden mit hohen Kohlendioxidgehalten, wie sie für CCS-Systeme typisch sind, auf der Basis der mit dem Auftraggeber benannten Messverfahren und Messmethoden festgelegt werden. In Abstimmung sollte eine geeignete Messstrecke ausgewählt werden um das Messsystem hinsichtlich seiner Eignung in ersten Versuchen zu testen.

Bis jetzt sind noch viele der in Erwägung zu ziehenden Methoden und Verfahren bzw. Techniken weder ausprobiert und getestet, noch erprobt und nachgewiesen worden. Die Regulierungsbe-hörden sind sich bewusst, dass das Wissen zur zuverlässigen Bewertung eines CCS-Programms gegenwärtig nicht vollständig vorliegt.

Beim Projektstart konnten keine selektiv geeigneten Messsysteme und Messverfahren benannt werden. Für die Ausstattung von potentiellen Messstrecken mit entsprechender Messtechnik standen keine zusätzlichen Mittel zur Verfügung. Die Aufgabenstellung wurde deshalb auf vorbereitende Schritte erweitert:

- Prüfung der technischen Voraussetzungen verschiedener Pilot-und Versuchsanlagen zur CO_2-Abscheidung sowie Industrieanlagen, an denen bereits vorhandene Messsysteme zur quantitativen Erfassung von CO_2-Strömen getestet werden können. Hierbei steht neben der Feststellung vorhandener Randbedingungen die an den Anlagen installierte Messtechnik im Fokus der vergleichenden Betrachtung.
- Kontaktaufnahme zu Messgeräteherstellern mit dem Ziel, dass Messgeräte zur Ergänzung von bestehenden Messsystemen an oben genannten Versuchsanlagen unentgeltlich zur Verfügung gestellt werden. Die konkrete Erfahrung der Hersteller mit CCS-Messbedingungen sollten zusammengefasst werden.
- Kontaktaufnahme zu TÜV SÜD NEL in Glasgow (UK) zur Prüfung von Möglichkeiten zur Durchführung von Tests (CO_2-Durchfluss- und CO_2-Konzentrationsmesssungen) an deren Versuchsanlage.
- Durchführung eines Vor-Ort-Termins bei TÜV SÜD NEL und Erarbeitung eines Versuchsprogrammes zusammen mit dem Auftraggeber (UBA)
- Beauftragung von TÜV SÜD NEL mit der Durchführung von Test-Programmen für CO_2-Durchfluss- und CO_2-Konzentrationsmesssungen an deren Versuchsanlage.

Nachfolgend sind die wesentlichsten Schritte des Projektverlaufes chronologisch aufgeführt:

- 08.11.2011: Kontaktaufnahme zur Universität Stuttgart, Institut für Kraftwerkstechnik (IFK) zur Prüfung von Möglichkeiten zur Durchführung von Labortests (CO_2-Konzentrationsmessungen) in deren Forschungslabor.

  Anm.: Die Aktivitäten mit der Universität Stuttgart (IFK) sind nicht Gegenstand dieses UFOPLAN Forschungs- und Entwicklungsvorhabens. Sie werden im Rahmen des Sachverständigengutachtens FKZ 390 01 025:

  „Evaluierung von Messeinrichtungen zur Quantifizierung von Kohlendioxid in typischen Restgasen industrieller Anlagen, Anlagen zur Energiewirtschaft und der Brennstoffaufbereitung“

  abgehandelt.

- 09.04.2012: Kontaktaufnahme zu TÜV SÜD NEL in Glasgow (UK) zur Prüfung von Möglichkeiten zur Durchführung von Tests (CO_2-Durchfluss- und CO_2-Konzentrationsmesssungen) an deren Versuchsanlage.
- 25.05.2012: Einreichung des 1. Zwischenberichtes (Sachstandsbericht 05/12) beim Umweltbundesamt
- 15.06.2012 Ortstermin bei TÜV SÜD NEL in Glasgow:

Im Rahmen dieses Vor-Ort-Termins wurde zusammen mit dem Auftraggeber (UBA) ein Versuchsprogramm für CO_2-Durchfluss- und CO_2-Konzentrationsmes-sungen erarbeitet und TÜV SÜD NEL mit der Durchführung dieses Versuchsprogramms das in 2 Arbeitspakete (Work Packages 1+2) aufgeteilt wurde, beauftragt.

WP1: Untersuchung von Durchflussmesssystemen für CO_2-Ströme

WP2: Untersuchung von Konzentrationsmesssystemen für CO_2

Die Tests bzgl. der Durchflussmesssysteme an der Teststrecke von TÜV SÜD NEL (Gasdurchfluss-Kalibrierungsschleife) sollten vergleichend durchgeführt werden, da es gegenwärtig keinen Primärstandard für Durchflussmessungen in flüssigem oder gasförmigem CO_2 gibt.

Aus den Versuchen waren Beiträge zur Unsicherheit von Messergebnissen in Bezug auf das für die Zulassung von kontinuierlichen Messeinrichtungen vorgeschriebene Eignungsprüfungsverfahren auszuwerten und die erreichbare Gesamtmessunsicherheit mit Blick auf die MVO abzuschätzen.

Aus den Erfahrungen sollten Empfehlungen für den Einsatz von kontinuierlichen Durchflussmesssystemen bei der Überwachung von CCS-Abgasen (und auch im Einsatz an Industrieanlagen zum Zweck der CO_2-Überwachung nach MVO) ausgesprochen werden.

Anm.: Die Durchführung von Work Package 1 erfolgte im Oktober 2012 an der Teststrecke von TÜV SÜD NEL, die Durchführung von Work-Package 2 war für Januar / Februar 2013, ebenfalls an der Teststrecke von TÜV SÜD NEL vorgesehen. Aufgrund technischer Schwierigkeiten war die Durchführung dieses Untersuchungspaket im vorgesehenen Zeitraum nicht möglich. Da nach Priorisierung durch den Auftraggeber ein Projektabschluss im Juni 2013 vorrangig war, konnte dieser Teil der Untersuchungen nicht durchgeführt werden.

- 18.09.2012: Die weitere Vorgehensweise sowie die ersten Ergebnisse des inzwischen gestarteten Testprogrammes für Durchflussmessungen bei TÜV SÜD NEL wurden in einem Abstimmungsgespräch im Umweltbundesamt erörtert.
- 16.11.2012: Einreichung des 2. Zwischenberichtes (Sachstandsbericht 11/12) beim Umweltbundesamt
- 05.06.2013: Einreichung des Schlussberichtes (Entwurf) im Rahmen eines Workshops beim Umweltbundesamt

Die kontinuierliche Emissionsmessung von Luftschadstoffen in Industrieabgasen wurde mit Einführung des Immissionsschutzes nach den Vorgaben immissionsschutzrechtlicher Regelungen betriebliche Praxis. CO_2 ist kein Luftschadstoff und deshalb keine überwachungspflichtige Abgaskomponente. Der Betreiber kann auf eignungsgeprüfte Messeinrichtungen zurückgreifen.

Der Einsatz von kontinuierlichen CO_2-Messeinrichtungen bei Industrieanlagen ist möglich. Die einsetzbare Messtechnik arbeitet zuverlässig mit eingeführten Verfahren zur Qualitätssicherung. Die Einhaltung der höchsten Ebene nach Monitoringverordnung ist nicht möglich. Die Messunsicherheit muss individuell für die Messeinrichtung ermittelt und gegebenenfalls optimiert werden.

Es liegen keine Prüfergebnisse von Durchflussmessgeräten vor, die im komprimierten Abgas eingesetzt werden können. Durch Vergleich von eingesetzten Messverfahren bei atmosphärischen Messungen wird hierdurch ein großer Fehlerbeitrag erwartet. Es besteht Untersuchungsbedarf und Weiterentwicklungsbedarf für die Gerätehersteller, insbesondere durch die aktuell im Juni 2013 in Kraft getretene DIN EN 16911-2 [11].

Der Unsicherheitsbeitrag durch die Kalibrierung liefert nach den ermittelten Ergebnissen einen geringen Beitrag zur Gesamtmessunsicherheit.

Der Einsatz von Konzentrationsmessungen im komprimierten, hochkonzentrierten CCS-Gas scheint mit geringerer relativer Messunsicherheit möglich. Die Probegasentnahme und Entspannung auf atmosphärische Bedingungen ist nicht untersucht. Der Anwendungsfall ist in Deutschland derzeit nicht gegeben und außerhalb Deutschlands uns nicht bekannt.

3 Preparatory Investigations

Task: Specification of a suitable measurement system based on the measurement processes and measurement methods specified by the Client.

Checking of the technical prerequisites at a laboratory scale on industrial plant and of pilot and test rigs for CO_2 separation on which measurements systems for the quantitative measurement of CO_2 can be designed and tested. The focus of the review is the determination of existing boundary conditions as well as the measurement systems technologies installed in plants.

Location: Laboratory tests

Industrial plant with CO_2 emissions (preferred)

Test installations for CO_2 separation from flue gases

Application: Atmospheric CO_2 (preferred)

Highly concentrated CO_2

Boundary conditions: Concentration range

Pressure range

Temperature range

Interferents (flue gas matrix)

As a preparatory measure for the implementation of the research project, we contacted various operators of test installations for the separation of CO_2 from flue gases and operators of industrial plant which emit atmospheric CO_2. During on-site meetings, we visited individual installations and examined the possibilities and conditions for inclusion of the installations into the research projects, in consultation with the operators. In addition, we again contacted selected manufacturers of measurement systems for concentration as well as flow measurement to gain an overview of the current situation of available measurement technology suitable for this task.

4 Results of the Preliminary Investigation

To find a suitable plant with suitable metrological equipment, we contacted several companies which operate pilot plants for CO_2 separation in Germany. We introduced our project during site meetings and were able to inspect the plant and measurement equipment. The suitability of the plant, the interest of the operator and the basic conditions for cooperation were discussed.

The measurement problems can be discussed openly with manufacturers of measurement equipment. They are, however, not prepared to provide measurement equipment for test purpose free of charge.

The operators of separation plant are open to discussions. However, it is not possible to access specific data from their research. A systematic evaluation of operator data is not possible.

In summary, it can be stated that the possibility of investigating the measurement equipment under realistic conditions for its use in conjunction with CCS is only partially present in Germany.

- There is no measurement section in a plant compressing separated CO_2 to high pressure.
- There is no concentration measurement equipment for CO_2 with a measurement range up to 100 vol. % which has been tested for suitability.
- There is no plant worldwide (according to TÜV SÜD NEL) carrying out flow measurements with quality assured results nor are there flow measurement systems which have been tested systematically for use in the high pressure area and in the supercritical region [1].
- There is no method for checking a measurement standard under high pressure conditions of use.
- It is not yet clear which special conditions could arise during compression and decompression for injection which would then have to be taken into account in the measurement method.
- It might be possible to investigate partial aspects in individual plant.

Note on the quantitative determination of CO_2 in a compressed CO_2 stream:

Based on the findings gained from the research and development project FKZ: 3710 41 315 we regard measurement in the compressed state as being problematic or even not practicable at present with the measurement systems currently available (current state of the art). We therefore recommend carrying out the measurements in an uncompressed, i.e. ambient pressure gas stream. In this case, a measurement of the gas composition before compression is recommended for decompressed gases (i.e. gases which were previously compressed) to check the discrimination of contamination and other gaseous components in the CO_2 gas stream.

In our view the task of the project as described in the invitation to tender and our offer cannot be carried out as planned as the development, in particular of flow measurement technology for CO_2 in the high pressure region is still at a very early stage. The technical capabilities of a test section in which the effect of the relevant parameters – gas composition, inhomogeneity due to interferents, transition phases from liquid to supercritical phase – could be tested for various measurement systems have still to be created.

Taking account of the actual objective of the project, the new question has to be put as follows: Which special features have to be taken into account for setting up measurement equipment, what conditions could adversely affect measurements and which solutions might be available?

To make progress, we therefore suggest that instead of focusing on a complete measurement system, we split the project into tasks which are capable of being investigated.

- Summary of the problems in compressed highly concentrated flue gas.
- Compilation of the standards requirements for quantification of measurement uncertainties and evaluation of measurement equipment.
- As a complete measurement system is not possible, initial investigations of this subject examine the following:
  - Flow measurement: tests on the TÜV SÜD NEL test rig.
  - Concentration: tests at TÜV SÜD NEL (on test rig).
  - Concentration: tests at Stuttgart University, IFK (at laboratory scale).
  - Sampling: experience by Linde.
- Combined evaluation of all results with assessment of overall uncertainties.
- Best practice guidance for setting up measurement systems.

The activities of TÜV SÜD NEL (test rig) and IFK of Stuttgart University (laboratory scale) in particular promise fundamental findings for the objective of the project.

Taking account of the common objective of this research and development project and the experts' opinion

FKZ 390 01 025: "Evaluation of Measurement Equipment for the Quantification of Carbon Dioxide in Typical Waste Gases from Industrial Plant, Power Industry and Fuel Preparation Installations"

running in parallel, the tasks have been divided between the projects in consultation with the Client.

The experts' opinion has its emphasis on the examination of concentration measurements and the tests at laboratory scale at the Department of Combustion and Power Plant Technology of Stuttgart University. The standards discussed form the basis for assessment for both projects.

5 Implementation of Research Programme

Cooperation partner for implementing the research and development project

5.1 TÜV SÜD NEL

Our subsidiary TÜV SÜD NEL, based in Glasgow in Scotland, has been investing in research on aspects of carbon capture and storage (CCS): In July 2012, three new test facilities were taken into operation to be able to carry out measurements linked to CO_2 separation and storage. CCS is researched intensively in the United Kingdom and the topic has a high priority for the British government.

There are several research projects in the United Kingdom which investigate sub-sea CO_2 storage.

Using their test facilities, TÜV SÜD NEL investigate issues associated with CO_2 transport from capture to storage. For this purpose, measurement equipment is tested and calibrated in their new laboratories to be able to make reliable statements on how effective various transport methods are.

Furthermore, TÜV SÜD NEL has compiled comprehensive theoretical analyses in studies reviewing the difficulty of measuring highly compressed CO_2.

With TÜV SÜD NEL, the research project was able to gain a partner who was capable of providing a test facility in which it was possible to carry out investigations of flow as well as concentration measurement systems.

A research programme consisting of 2 work packages (Work Packages 1+2) was agreed together with TÜV SÜD NEL in consultation with the Federal Environmental Office:

WP1: Examination of flow measurement systems for CO_2 flows

WP2: Examination of concentration measurement systems for CO_2

Description of work package 1 (WP1):

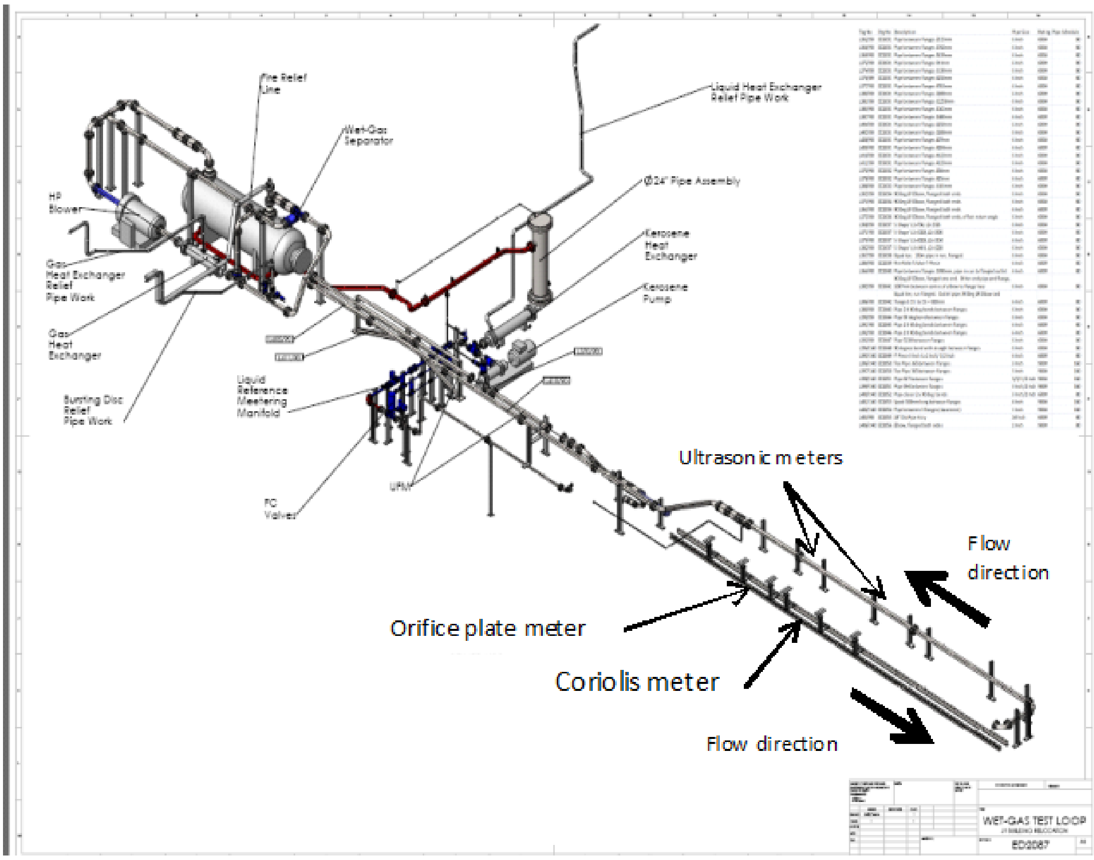
Examination of the operating behaviour of flow meters during the transport of gaseous CO_2

The quantitative measurement (mass concentration) of CO_2 depends on two specific measurements: the measured quantity (volume or mass) and the density, to enable a conversion of the volume measurement into a mass concentration. The density is the derived from the equation of state from temperature, pressure and gas composition.

The flow tests were carried out in NEL's wet gas test loop. This facility is designed for operation with dry gases such as N_2 or CO_2 or with wet gases, i.e. N_2 with kerosene or water addition.

The test equipment was operated in the dry gas mode, filled with CO_2 and a CO_2 / N2 mixture and operated until the pressure required was reached. The required flow rate was achieved by setting the blower output. The flow meters can be installed either in the main measurement section or in the return line. For these comparative tests, an orifice plate meter and a Coriolis meter (both with a nominal diameter of 200 mm) were installed in the main test section and the two 150 mm ultrasonic meters were installed in the return line

Figure 1: Test loop in the test facility at TÜV SÜD NEL



Source: TÜV SÜD NEL

The comparative tests were carried out for a flow range which was limited by the blower output and the pressure loss in the system. It was assumed that a maximum flow rate of 900 m^3/h could be achieved. A number of flow rates were determined during each test corresponding to the operating behaviour of the meters and the limitations of the blower output.

The tests were carried out at nominal pressures of 20 bar(a) and 15 bar(a). Mixtures of CO_2 in nitrogen with CO_2 concentrations of 100 % vol., 90 % vol. and 80 % vol. were used. The gas concentrations were determined by calculation from the pressure conditions and were confirmed by analyses if possible.

Flow rate, volume flow and sound velocity were recorded by the ultrasonic meters. Additional diagnostic data, such as signal strength and quality, were also recorded (assuming that the manufacturer had provided the appropriate diagnostic software). The mass flow rate was measured by the Coriolis flow meter, while the differential pressure measurements made it possible to calculate volume flow and mass flow from the orifice plate. The density was derived from temperature, pressure and gas composition via an equation of state.

5.2 Stuttgart University (IFK)

Stuttgart University (IFK) was subcontracted by TÜV SÜD to carry out investigations to comprehensively test CO_2 concentration measurement using NDIR. The work was carried out from 18.06.2012 to 14.12.2012.

These tests were supplemented by our own functional tests of the CO_2 measuring equipment used.

Note: The work with Stuttgart University (IFK) is not the subject of this UFOPLAN research and development project. It is dealt with in the experts' opinion FKZ 390 01 025:

"Evaluation of Measurement Equipment for the Quantification of Carbon Dioxide in Typical Waste Gases from Industrial Plant, Power Industry and Fuel Preparation Installations"

6 Emissions Monitoring Concept

6.1 General

The requirements for continuous emissions monitoring of industrial plant are stipulated in statutory regulations and are implemented and specified in detail by the relevant authorities in the approval documents for individual plants. To ensure that the results of measurements are robust and provide legal security, procedures are required for the quality assurance of automated measurement systems (AMS) which ensure that the requirements stipulated for the uncertainty of results are met.

To achieve this objective, three different quality assurance levels (QAL1, QAL2 and QAL3) have been set. The quality assurance levels comprise the suitability of the automatic measurement system for the measurement task (for example before or during procurement of the measurement system), validation of the AMS after installation and monitoring during the operation in the industrial plant. In addition, an annual surveillance test (AST) has been stipulated. The European Standard EN 14181 [2] describes the quality assurance procedures required and stipulates the statistical calculation methods for the evaluation of uncertainty. EN 14181 deals with the measurement of waste gas compositions, while standard EN ISO 16911-2 [3] derived from it details the quality and test criteria for the measurement of waste gas volume flows. As the standard for volume flow was developed mainly for emissions monitoring of waste incinerators, it can be applied fully only to atmospheric measurements. EN ISO 16911-2 deals with the requirements of the Monitoring and Reporting Regulations and details criteria for the minimisation of measurement uncertainties of the annual average for mass flows as the basis for the assessment of whether the quality tier requirements have been met.

In the following text, EN ISO 16911-2 is mentioned explicitly where the differences in contents of these two standards have to be brought out.

The procedures for emissions monitoring of stationary plant for the purpose of air pollution control are also to be applied to the monitoring of CO_2 emissions for greenhouse gas emissions trading when continuous emissions measurement systems are used for this.

6.2 Monitoring ans Reporting Regulations

The Monitoring and Reporting Regulations EU 601-2012 [4] require the use of measurement methods for emissions monitoring for all emissions of N_2O and for all transferred CO_2 emissions. Emission sources of more than 5,000 t CO_2 annually or of more than 10% of the total annual emissions of the installation shall meet the highest tier. For all other sources the operator may deviate by 1 tier from the tier to be adhered to. The operator may deviate by 1 tier only if he can demonstrate that adherence to the prescribed tier is technically not feasible or would lead to unreasonable costs and that calculation methods are also technically not feasible or reasonable. As a minimum, tier 1 must be observed. The tiers correspond to the following maximum measurement uncertainties to be observed for the mass flow of the emission source:

Table 1: CEMS measurement uncertainties in accordance with the Monitoring and Reporting Regulations (MRR)

	Tier 1	Tier 2	Tier 3	Tier 4
CO_2 emission source	± 10 %	± 7.5 %	± 5 %	± 2.5 %
N_2O emission source	± 10 %	± 7.5 %	± 5 %	n/a
CO_2 transfer	± 10 %	± 7.5 %	± 5 %	± 2.5 %

Source: Regulation EU 601-2012 (MRR)

All measurements shall be carried out in accordance with methods which conform to the above EN standards together with DIN EN 14181. The relevant testing and calibration of equipment shall be carried out by laboratories which are accredited for the analysis methods concerned.

The annual emission mass flow is calculated from the individual hour values for concentration and quantity of the waste gas. The operator may also generate shorter reference periods. If correction or reference calculations are required to integrate these measured values, these have to be made for every hourly value. Every reference period is valid if at least 80 % of the hourly average has been formed with valid measured signals. Otherwise the complete hourly value has to be regarded as invalid and has to be accounted for in the annual emission by means of the substitute value. The substitute value determined by the operator must be representative for the lost period.

Figure 2 on page 38 describes the evaluation and system for forming substitute values in accordance with the MRR.

For emission sources which are not related to N_2O from nitric acid plants or the transfer into a transport network or a storage site, the operator calculates the same emissions as from a nitric acid plant without using uncertainty values to support the emission measurement as a plausibility check.

Figure 2: Emission analysis in accordance with the Monitoring and Reporting Regulations (MRR)

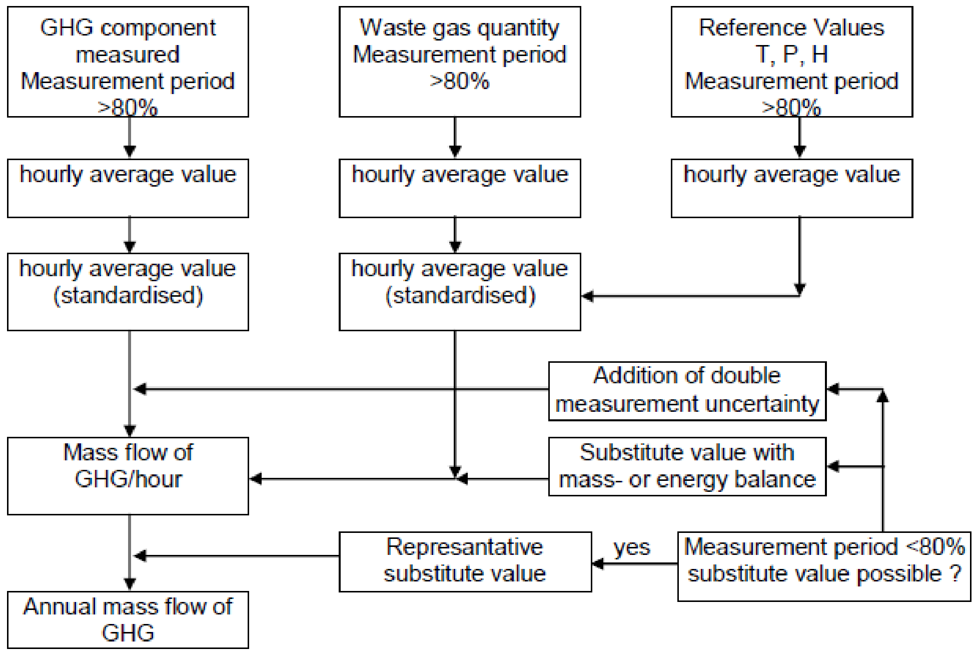
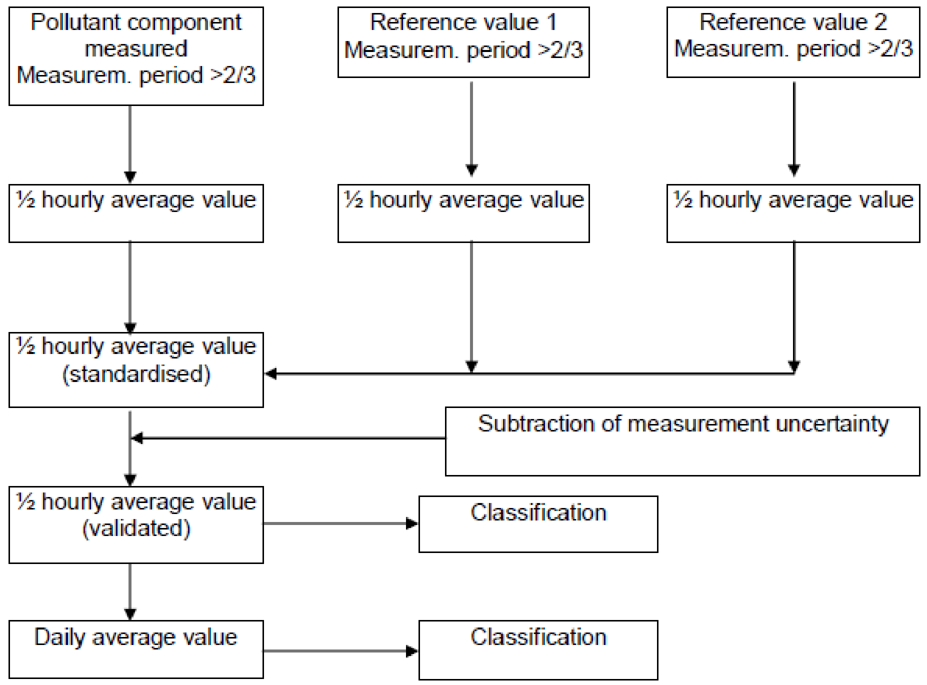


Diagram: TÜV SÜD Industrie Service GmbH

Figure 3: Emission evaluation in accordance with the German Immission Control Act



6.3 Suitability test (QAL1)

The determination of the suitability of automatic measurement equipment and the measurement method is dealt with in EN 15267-3 [6] and EN ISO 14956 [7]. The procedure described therein is based on the calculation of the total uncertainty of the values measured with the automatic measurement equipment. This total uncertainty is calculated taking account of those contributions to uncertainty which are caused by individual process parameters of the measurement equipment which contribute to uncertainty.

DIN EN 15267-3 is the standard for the certification of automatic measurement equipment for the monitoring of emissions from stationary sources. This product certification encompasses the following four consecutive steps:

- suitability test of an AMS;
- first assessment of the quality management system of the AMS manufacturer;
- certification;
- monitoring of the manufacturing process after certification.

The manufacturer of the measurement equipment must have the measurement equipment certified by a body accredited for suitability tests in accordance with EN 17025 [8].Successful certification is proof that the measurement equipment is suitable for the measurement task and a fundamental condition for it to be used for emissions monitoring in accordance with the official requirements for approval.

EN 15267-3 stipulates minimum requirements and test procedures for automatic measurement equipment for the measurement of gases in waste gas from stationary sources and for the measurement of the waste gas volume flow. This European Standard is the basis for the requirements of certain EC guidelines. It provides detailed procedures for the implementation of the requirements of the first quality assurance level (QAL1) of EN 14181 and, if required, the input data for the third quality assurance level (QAL3).

It describes a combination of laboratory and field tests. Testing in the laboratory permits an assessment as to whether the AMS can maintain the relevant minimum requirements under controlled conditions. The field test, over a period of at least three months, is designed to assess whether the AMS can maintain the relevant minimum requirements in continuous operation under real operating conditions. Field testing is carried out on an industrial process representative of the intended application of the AMS for which the manufacturer seeks certification. The process characteristics of an AMS in connection with the monitoring of concentration measurements are:

Table 2: Process parameters for concentration measurement

Laboratory test process parameters Concentration	Minimum Requirements	
	Gases (except O_2)	O_2
Response time	✥ 200 s	✥ 200 s
Repeatability (standard deviation) at zero	✥ 2.0 % a	✥ 0.20 % b
Repeatability (standard deviation) at span	✥ 2.0 % a	✥ 0.20 % b
Lack of fit (linearity)	✥ 2.0 % a	✥ 0.20 % b
Effect of the ambient temperature change from the nominal value at 20°C within a specified range at zero point	✥ 5.0 % a	✥ 0.50 % b
Effect of the ambient temperature change from the nominal value at 20°C within a specified range at span point	✥ 5.0 % a	✥ 0.50 % b
Effect of the sample gas pressure at span point for a pressure change ←p of 3 kPa	✥ 2.0 % a	✥ 0.20 % b
Effect of the sample gas flow on extractive AMS for a given value specified by the manufacturer	✥ 2.0 % a	✥ 0.20 % b
Effect of the mains voltage at -15 % below and +10 % above the nominal supply voltage	✥ 2.0 % a	✥ 0.20 % b
Effect of vibration	✥ 2.0 % a	✥ 0.20 % b
Cross-sensitivity	✥ 4.0 % a	✥ 0.40 % b
Excursion of the measurement beam of in-situ AMS	✥ 2.0 % a	-
Field test process parameters		
Correlation coefficient of calibration function R2	✥ 0.90	✥ 0.90
Response time	✥ 200 s	✥ 200 s
Lack of fit	✥ 2.0 % a	✥ 0.20 % b
Minimum maintenance interval	8 days	8 days
Zero drift within maintenance interval	✥ 2.0 % a	✥ 0.20 % b
Span drift within maintenance interval	✥ 2.0 % a	✥ 0.20 % b
Availability	✥ 95.0 %	✥ 98.0 %
Reproducibility Rfield	✥ 3.3 % a	✥ 0.20 % b

a Percentage value as percentage of the upper limit of the certification range

b Percentage value as oxygen volume concentration (volume fraction)

Source: EN 15267-3

The process parameters of an AMS in connection with the monitoring of volume flow measurements are:

Table 3: Process parameters for volume flow measurement

Laboratory test process parameters Volume flow	Minimum requirements
Response time	✥ 60 s
Repeatability (standard deviation) at the defined minimum flow rate	✥ 2.0
Repeatability (standard deviation) at the defined maximum flow rate	✥ 2.0 %
Lack of fit (linearity)	✥ 3.0 %
Effect of the ambient temperature change from the nominal value at 20 °C within a specified range at zero point	✥ 5.0 %
Effect of the ambient temperature change from the nominal value at 20 °C within a specified range at span point	✥ 5.0 %
Effect of the mains voltage at -15 % below and +10 % above the nominal supply voltage	✥ 2.0 %
Effect of vibration	✥ 2.0 %
Assessment of QAL3 control capability	pass
Assessment of linearity control capability	pass
Field test process parameters	
Correlation coefficient of calibration function R2	✥ 0.90
Response time	✥ 60 s
Minimum maintenance interval	8 days
Zero drift within maintenance interval	✥ 2.0 %
Span drift within maintenance interval	✥ 4.0 %
Availability	✥ 95.0 %
Reproducibility Rfield	✥ 3.3 %

Source: EN 15267-3, supplemented by EN 16911-2

The uncertainties determined during the laboratory and field tests shall be used for calculation of the combined standard uncertainty of the AMS measured values in accordance with EN ISO 14956. Either the repeatability in the laboratory or the reproducibility in the field is to be used to calculate the standard uncertainty. The larger of the two values of these two parameters shall be used. In addition to the contributions to uncertainty of the measurement equipment tested, EN ISO 14956 permits taking account of external input quantities (e.g. measured values of other parameters which are determined with the equipment in the plant and are used for conversion to standard conditions) for the calculation of the combined standard uncertainty to EN ISO 14956.

The following uncertainty contributions from EN 15267-3 are combined when determining the combined uncertainty QAL1 of the measurement equipment:

- Linearity
- Zero drift from field test
- Span drift from field test
- Effect of ambient temperature at span
- Effect of sample gas pressure (not relevant for extractive measurements)
- Effect of sample gas volume flow
- Effect of mains voltage
- Cross-sensitivity
- Repeatability standard deviation at span (alternative)
- Standard deviation from paired measurements under field conditions (alternative)
- Uncertainty of the reference material or reference method provided by the manufacturer (indirect volume flow determination by, for example, differential pressure, ultrasound speed etc.)
- Any other uncertainties inherent in the equipment which are not covered by the span check (for volume flow)

Of the two contributions marked as alternative that with the higher value is used for the calculation. The total uncertainty is given by:

$$u_c = \sqrt{\sum_{i=1}^{N} u_i^2}$$

The total uncertainty of the AMS determined from the tests according to this standard should be at least 25 % below the maximum permissible uncertainty specified in the applicable legal regulations. If no limits are specified for the component, reference is made to the certification range (tested measurement range) as an alternative. A sufficient margin for the uncertainty contributions from the individual installation of the AMS is necessary to pass QAL2 and QAL3 of EN 14181 successfully.

6.3.1 Preliminary investigation, calibration (QAL2) and annual surveillance test (AST)

When an AMS is newly installed, it must have certification to EN 15267-3. The installation location must meet the requirements of EN 15259 for measurement sections and measurement sites.

6.3.1.1 Preliminary investigation

Equipment for the measurement of volume flow require a preliminary investigation in accordance with the requirements of EN 16911-2 to characterise the flow so that the AMS can be located at a position where changes in the flow profile do not have an adverse effect on the performance of the AMS. The preliminary investigation also enables the operator to determine whether point, line or grid measurements will meet the uncertainty requirements of this standard.

The main concern with regard to the calibration of volume flow measurement equipment is the stability of the flow profiles when the plant operating conditions change. If the flow profile changes when the load conditions of the plant change, flow controllers are operated or different waste gas duct inlets come on stream, this has to be taken into account for the decision on the type of volume flow AMS to be installed and for calibration. The dominant source of systematic measurement errors is the change in the flow profile. The main cause of changes in the flow profile are changes in the restrictions in the waste gas duct or large changes in the volume flow. Their effect is greater the lower the flow velocity is.

During the preliminary investigation, the main characteristics of the flow profile at the planned installation position of the AMS are to be determined and it has to be ascertained whether changes in the profile are to be expected and how severe their effect on the calibration function is. In case of predictable flow profiles a preliminary investigation is not necessary; in this case an extended calibration procedure has to be applied for later QAL2 and AST calibrations.

The preliminary investigation can be by measurement or CFD:

6.3.1.2 Preliminary investigation by measurement

The preliminary investigation must consist of at least two measurements which are carried out in accordance with EN 16911-2 and determine the flow profile in the primary measurement axis and an axis perpendicular to it. Both measurements have to be carried out for two different plant operating conditions:

- one where the most uniform flow profile is to be expected, i.e. near the highest flow velocity and the least obstruction of the flow path;
- one where the flow velocity is so low that it is exceeded during at least 90 % of plant operation, in combination with the largest obstruction of the flow path, e.g. by closing of dampers and flow conditioners.

From these two measurements the reproducibility of the standardised flow calculated for each measurement plane and the Crest factor *) as well as skewness are to be calculated for each of the 4 profiles.

*) The Crest factor or ratio of peak value to average value is a measure for a flow profile calculated from the peak value measured for the profile divided by the average value of the profile in the primary and secondary measurement plane.

6.3.1.3 Selection of the automated measurement system

The plant operator can select the measurement method of the automated measurement system based on the results for reproducibility, skewness and crest factor using the table below.

6.3.1.4 Preliminary investigation using CFD

Computational fluid dynamics is an accepted method in flow physics for the preliminary investigation of flow conditions in a waste gas duct or a pipeline. CFD requires precise data on the path and the geometric dimensions of the duct system including the upstream section. In addition, important fundamental design parameters have to be taken into account (e.g. number and position of waste gas inlet ports, plant load and gas velocity range). The flow is modelled on the basis of this information using special software. The results of the computer simulation are processed and are evaluated with 2 or 3 dimensional diagrams from which flow profiles can be generated.

6.3.1.5 Selection of the automated measurement system

The plant operator can select the measurement method of the automated measurement system based on the results for reproducibility, skewness and crest factor using the table below.

Table 4: Skew and crest factor from preliminary investigation

Reproducibility of normalised profile	Crest factor	Skew-ness	Measurement method	Comments
< 5.00 %	< 1.30	< 1.20	One-sided probe with point measurement or limited path length	Changes in the flow profile are unlikely.
> 5.00 %	< 1.30	< 1.20	1 cross duct monitoring path or a one-sided probe with limited path length in smaller waste gas ducts	The flow profile is expected to change with the flow rate.
	> 1.30	> 1.20	1 cross duct monitoring path in the plane with the greatest skewness	The flow profile is expected to change with the flow rate, but there is no swirl.
	> 1.30	> 1.20	2 cross duct monitoring paths along the primary and secondary monitoring paths	A skewed flow profile with swirl, i.e. the point in the profile with the maximum flow rate is rotating and the best way to secure a representative average is to monitor in a cross or across two chords.

6.3.2 Calibration and surveillance test

The second quality assurance level comprises the determination of the calibration function and its variability as well as an examination of the variability of the values measured by the AMS by comparison with the uncertainties specified in law. Testing under QAL2 is carried out on suitable AMS which have previously been correctly installed and commissioned. Calibration is preceded by a surveillance test. The surveillance test considers the following criteria:

- Alignment and cleanliness of the sampling equipment
- Documentation and records
- Serviceability
- Leak test
- Zero and span check
- Linearity
- Cross-sensitivity
- Zero and span drift (QAL3 audit)
- Response time

For volume flow measurements, the configuration of the measurement equipment and the geometric configuration including measurement of the waste gas duct cross-section must also be recorded. All measurement equipment shall also be tested for reference quantities.

During calibration, at least 15 measurements shall be made using a standard reference method (SRM) over a period of 3 days (volume flow for 1 day equal to 6 hours). From the measurements of the automatic measurement equipment 15 pairs of values are obtained (9 pairs for volume flow with preliminary investigation) which are evaluated statistically. The value measured by the AMS shall be calculated for each measurement using the calibration function. A plant-specific calibration function is set up for the measurement component and variability sD is calculated as reproducibility in accordance with the statistical method from EN 14181. This must not exceed the maximum uncertainty specified for the component measured with a statistical certainty of 95%. For volume flow calibrations, the maximum uncertainty is 2 % of the measurement range extrapolated to 120 % of the maximum value.

Calibration of measurement equipment using the standard reference method (SRM) accounts for the effects of the place of measurement and the installation of the measurement equipment. Moreover, the effect of plant-specific waste gas conditions and other components (matrix effect) as well as running and operating conditions of the plant is included.

The results determined with the SRM have to be stated under the same conditions as those which were measured by the automatic measurement equipment which corresponds to the unit m/s for volume flow.

An annual surveillance test (AST) is carried out to check the measurement equipment and the validity of the calibration function. The AST also includes a functional test and 5 comparative measurements over one day (4 for volume flow with preliminary investigation) which confirm the validity of the calibration function if the variability corresponds to the requirements.

Calibration and surveillance test may be carried out only by competent laboratories accredited to EN ISO 17025. The calibration shall be carried out anew after major changes to the plant operation, after repair of the AMS or on the basis of legal requirements and shall otherwise be repeated regularly (after 3 years at the latest).

If the surveillance results are used for reports on greenhouse gas emissions, the QAL2 and AST reports must include an assessment by the testing laboratory of the capability of the volume flow monitoring equipment to provide a true annual average of the mass flow.

6.4 Ongoing quality assurance during operation (QAL3)

The AMS can drift or become less precise during routine operation. Drift or instability can be due to changes in the AMS, for example contamination of an optical surface, gradual failure of a component or blockage in a filter. Such changes can cause systematic deviations in the AMS data. On the other hand, AMS are subject to short-term variations in stability and precision due to factors such as changes in ambient temperature. These variations can cause random deviations. The magnitude of the random deviations is assessed during the certification process of the AMS (QAL1).

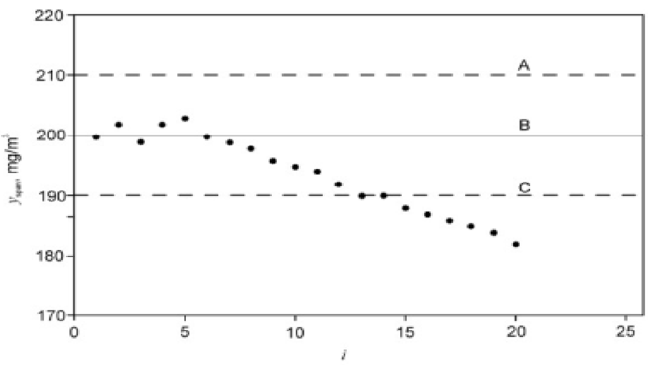
After the acceptance and calibration of the AMS, further quality assurance and quality control procedures shall be followed so as to ensure that the measured values obtained with the AMS meet the stated or required uncertainty during continuous operation. The implementation and performance of the QAL3 procedures given in EN 14181 are the responsibility of the plant owner.

The aim of the procedure is to maintain and demonstrate the quality of the AMS so that the requirement for the stated zero and span repeatability and drift values are met during ongoing operation and the AMS is maintained in the same operational condition as when installed and calibrated under QAL2. This shall be achieved by continuously checking the deviations determined in QAL1 in tests with a reference material (e.g. a test gas) using control charts which record the zero and span drifts and determine systematic or random deviations outside specified limits. If the limits are exceeded, the AMS is out of the control range and must be readjusted. If an adjustment is not possible or successful, the AMS must be repaired.

The internal reference point measurements of QAL3 must be carried out at intervals no greater than the maintenance interval, as specified during the type test in accordance with EN 15267-3.

In accordance with EN 14181, different control charts may be used. The most suitable control chart for the conditions of use can be chosen. All control charts have the purpose of maintaining the control range during operation so that the uncertainty contribution specified in QAL1 is not exceeded.

Figure 4: Example of a Shewhart control chart



Key

y'_{span} span value, in milligrams per cubic metre (mg/m³)

i number of span check, with i = 1 to n

A upper action limit

B baseline

C lower action limit

Source: Draft EN 14181:2012

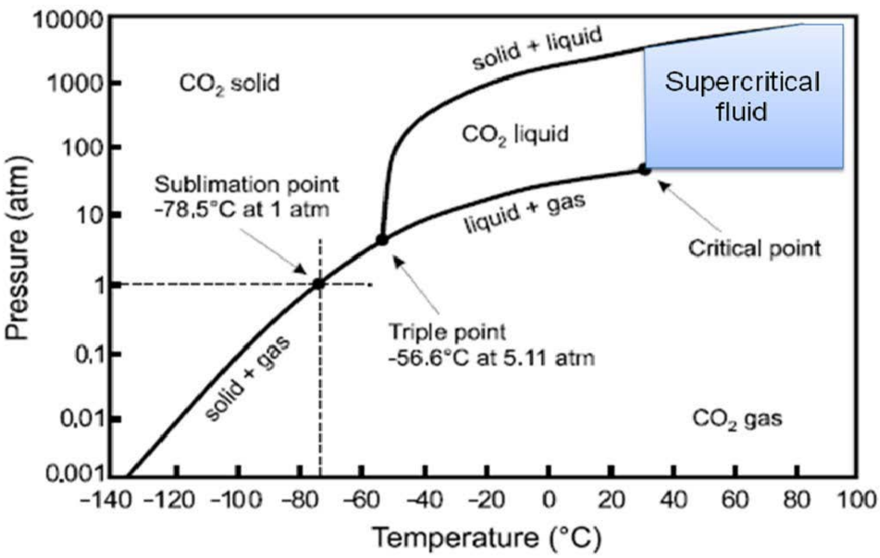
6.5 CO_2 phase diagram

The captured CO_2 can be transported in pipelines as well as containers for road, sea and rail transport. The transport requirements and methods depend on the site of the power station and the CO_2 storage site. Transport of CO_2 for large-scale industrial use of CCS in commercial power stations will take place in a highly compressed state, mainly via pipelines.

Transport in pipelines

The supercritical or the liquid phase is preferred for the transport of CO_2 in pipelines. In the gaseous phase, CO_2 has too low a density to be able to transport it economically in pipelines. CO_2 in the supercritical or liquid phase has a higher density and therefore a larger mass can be transported for a given pipeline diameter. At pressures above 73.8 bar, CO_2 is present in the supercritical phase for temperatures above 31.0 °C. At pressures above the critical point and temperatures below 31.0 °C, CO_2 is present in the liquid phase.

Figure 5: Phase diagram of carbon dioxide



Source: TÜV SÜD NEL

Pipelines for the transport of supercritical CO_2 must be able to withstand pressures up to 200 bar. Temperature and pressure fluctuations can present difficulties with the transport in pipelines over long distances. This can lead to a change of state of the fluid between solid, gaseous, liquid and supercritical. Temperature and pressure fluctuations can also lead to the occurrence of a multi-phase system in the pipeline.

6.6 Measurement principles and setups of volume flow measurement systems

To determine the captured CO_2 streams for CCS applications, precise measurement of the volume flow is necessary in addition to the determination of the concentration. For this reason, various techniques are described below which are suitable for or are being used for CCS applications.

6.6.1 Orifice plate measurement (differential pressure)

For differential pressure measurement, two pressures P1 and P2 are compared and their difference is determined, $\Delta P = P1 - P2$.

In a pipe with a uniform flow, an orifice plate causes a reduction in the cross-section. At the point of restriction, the flow velocity increases and the static pressure decreases, as described by the flow theorem according to Bernoulli and Venturi. This pressure drop is recorded by a differential pressure meter. The orifice plate is thus only a “tool” to produce a pressure drop at a defined point in a pipe.

The volume flow can be calculated if density, viscosity, temperature and the isentropic exponent, which can be determined using additional measurement equipment, are known.

Figure 6: Differential pressure measurement using an orifice plate

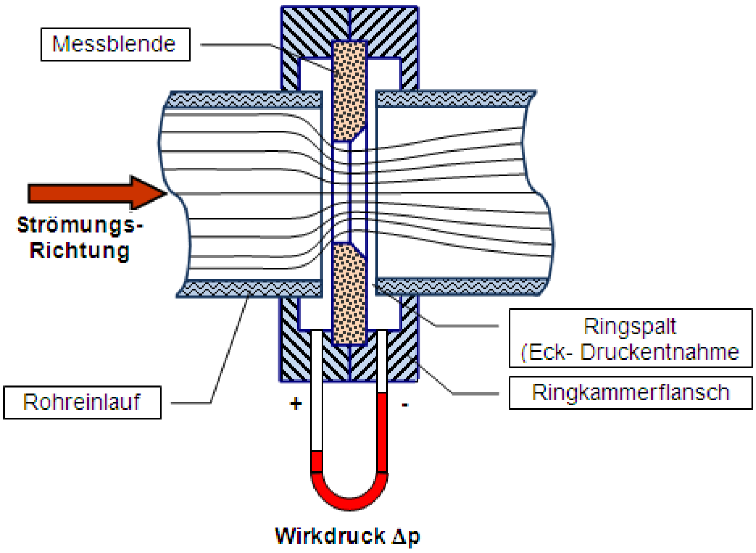


Figure: TÜV SÜD Industrie Service GmbH

Orifice plates are the most frequently used method for determining flow in power stations. If density and viscosity of the fluid are known, it is possible to achieve highly accurate measurements. For flow, in ordinary steady state single phase CO_2, a measurement uncertainty of ± 1% of the measurement range is claimed.

In addition, orifice plates can only be used in single phase systems, either gaseous, liquid or supercritical. This assumes that the orifice plate is fitted at a point where the phase present is known and that phase transitions can be excluded.

As with other types of flow measurement, orifice plates require large upstream and downstream straight pipe lengths to ensure that ideal flow conditions are present for accurate measurement.

6.6.2 Ultrasonic flowmeters

Ultrasonic flowmeters (USMs) measure the velocity of a flowing medium (gas, liquid) using acoustic waves. Two main measurement principles are used for the acoustic flow measurement using ultrasound in industrial plant. They are the ultrasonic Doppler method and the ultrasonic time-of-flight (ToF) method.

The ultrasonic Doppler method can be further divided into the Doppler method and the stroboscope method. Neither of these methods will be discussed any further as both methods require particles in the flowing medium to determine flow and these are highly unlikely to be present in a very pure, highly concentrated CO2 gas stream.

The ultrasonic time-of-flight method can be divided into two further sub-groups:

- Drift method

For the drift method, a continuous ultrasonic signal is transmitted perpendicular to the flow of the medium to be measured. The intensity distribution will be deflected by the medium according to the direction of flow. The relative flow velocity can be determined from the relative intensity distribution of the ultrasonic signal at the opposite receiver.

- Time-of-flight measurement

The medium should be as homogenous as possible and only contain a low percentage of solid particles. A sound wave propagates faster in the direction of flow of the medium to be measured than a sound wave in the opposite direction.

The propagation times are measured continuously. The difference in time of flight of the two ultrasonic waves is thus directly proportional to the average flow velocity.

The flow volume per time unit is the result from the average flow velocity multiplied by the pipe cross-section of the detector. The medium to be measured can be identified directly from the time of flight of the ultrasonic waves.

Figure 7: Ultrasonic time-of-flight measurement

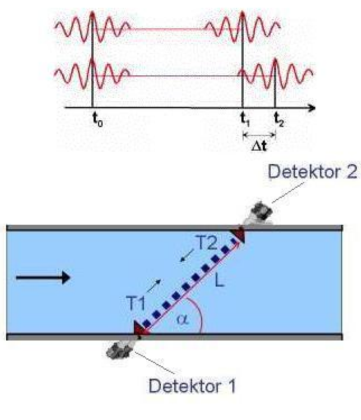


Figure: TÜV SÜD Industrie Service GmbH

- Clamp On

Both of the above methods are used by various manufacturers. There is also a special type in which the equipment is not integrated into the pipe, but clamped on. This has the advantage that nothing has to be inserted into the pipe itself and thus that there is no pressure loss, and the device can be installed at a later date at a low cost.

Figure 8: Clamp On ultrasonic measurement

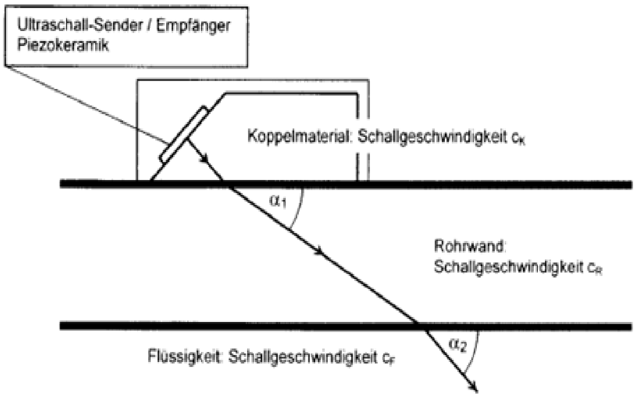


Figure: TÜV SÜD Industrie Service GmbH

ToF meters are used extensively for fiscal and custody transfer applications in both liquids and gases. However, no references have been found for their use in CCS applications in the supercritical phase. CO_2 gas gives significant problems in measurement using ultrasonic meters. Gaseous CO_2 effectively absorbs ultrasound making signal resolution extremely difficult. However, a high-resolution signal is required to achieve a high accuracy of measurement.

When operating in the supercritical region where the density may be variable, the frequency of the transmitter required to maximise the signal may exceed the measurement range available. The wall thickness that the ultrasonic signal of a clamp-on meter can penetrate must still be investigated.

To carry out an accurate volumetric flow rate measurement, a correction of the flow profile is required. This can be derived from density and viscosity measurements. The density is also required to derive the mass flow. Despite these difficulties, ToF-based ultrasonic flowmeters show potential for providing the basis for a high accuracy measurement system. However, extensive development will be required for this. In addition, the use of ultrasonic measurements can give information on density and possibly gas concentration, through calculations based on the output signal.

6.6.3 Mass flowmeters

Coriolis principle

The mass flowmeter based on the Coriolis principle consist of two metallic tubes; however, the latest generation only has one tube. The U-tube is vibrated during operation. The vibration frequency is constant if there is no flow. When there is flow, the vibration of the U-tube changes due to the Coriolis force. The density of the flowing medium can be calculated as a side effect of this self-resonant behaviour via the frequency of the output signal. The measurement tube frequency is inversely proportional to the density.

Figure 9: Coriolis mass flow meter

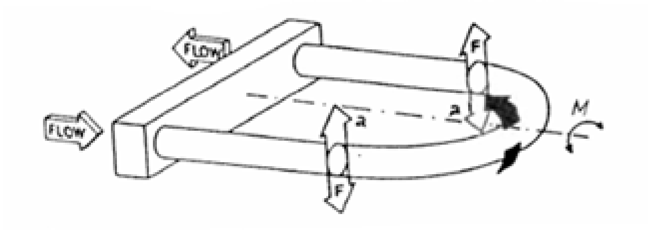


Figure: TÜV SÜD Industrie Service GmbH

Coriolis meters work reliably in dense phase / supercritical phase ethylene applications for custody transfer. A Coriolis meter will remain undamaged by changes in fluid phase (although liquids will give problems) and hence should be able to operate across the full range of phase conditions that may occur in CCS applications.

The main advantage to CCS applications is that Coriolis flowmeters provide a mass flow measurement plus additional measurements of temperature and density to characterise the condition of the gas in the pipeline. The main drawback is that Coriolis flowmeters are currently limited to pipeline diameters of 150, 250 and 300 mm.

6.7 Data processing

Data recording and data processing units were connected to the measurement equipment. These recorded the electric output signals of the measurement equipment. The condition of the measurement equipment was also monitored via digital outputs. Signals typical for this are:

- Flow problem (e.g. increased flow resistance due to contamination)
- Temperature monitoring
- Error message via electronic self-monitoring of the measurement system

The analyser receives data via the digital outputs which provide information on whether the equipment signal is valid or not. An error signal informs the operator that immediate action is required to remove the fault. The control chart function as per QAL3 may also be integrated into the analyser.

The analysers for continuous emissions monitoring are also subject to a suitability test. In Germany, the test criteria are based on the circulars of the German Environment Ministry of 13.06.2005 – File Ref. IG I 2 - 45053/5 – and of 04.08.2010 – File Ref: IG I 2- 51134/0 (both regarding the Uniform Nationwide Practice for Monitoring Emissions) – and on EN 15267 regarding the implementation of a field test.

The Uniform Nationwide Practice for Monitoring Emissions does currently not include any of the requirements of the MRR, but only the legal requirements to monitor emissions from stationary sources in accordance with the requirements of the 13th, 17th and 27th German Immission Control Ordinance and TA Luft (Technical Guidelines for Air Pollution Control).

6.8 Determination of the total error of the measurement method

6.8.1 Error component due to fluctuations during continuous operation

The suitability test of measurement equipment determines whether this meets 75 % of the maximum uncertainty required by law with reference to the emission limits. The total error is made up of the individual error contributions and refers to the total envelope tested which corresponds to all possible realistic operating conditions. The individual errors listed in the suitability test are adjusted to the possible fluctuation range at the actual place of installation by specific calculation of the control chart limits.

While this calculation applies the process characteristics from the suitability test, the plant operator must take account of the actual plant conditions. During a test to EN 15267-3 within the scope of QAL1, the effect of the ambient temperature on the AMS within a specified range, for example 5 °C to 40 °C, is examined. However, if the AMS is situated in an air-conditioned housing in which the temperature varies between 18 °C and 23 °C, the operator uses a temperature spread of 5 °C when calculating sAMS. If an effect is time-dependent, this has to be taken into account. If, for example, the instability is stated as a percentage ±p over q days, then q corresponds to the time between two readings for the control chart.

The standard deviation sAMS as per EN14181 has to be calculated as follows:

$$s_{AMS} = \sqrt{u_{inst}^2 + u_{temp}^2 + u_{volt}^2 + u_{pres}^2 + u_{others}^2}$$

Where

uinst is the uncertainty due to instability;

utemp is the uncertainty due to variations in ambient temperature;

uvolt the uncertainty due to variations in voltage;

upres the uncertainty due to variations in ambient pressure;

uothers is any other uncertainty which may affect the reading on zero and span reference material (e.g. dilution).

Systematic and random deviations during long-term continuous operation of measurement equipment should be within the total error from the suitability test when applied to the real operating conditions.

6.8.2 Error component due to variability from calibration

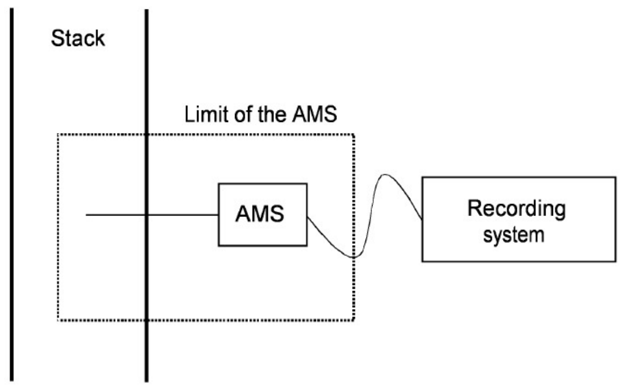
During calibration of measurement equipment the repeatability is determined by parallel measurements with an independent standard reference method. The calculated variability includes all error effects of the measurement location and the installation of the measurement equipment, of plant-specific waste gas conditions and of operation and operating conditions of the plant. Comparative measurements are to be carried out for all normal operating conditions of the plant to obtain a representative calibration function and variability.

The calibration is carried out over a short period of 3 days. The error determined does not contain long-term variations due to the operating conditions of the measurement equipment.

6.8.3 Error component from data acquisition and recording

EN 14181 is limited to quality assurance of automatic measurement equipment and does not include the quality assurance of data acquisition and recording systems of the plant.

Figure 10: Limits of quality assurance of AMS excluding the data acquisition system



Source: Draft EN 14181:2012

6.9 Total error calculation

The total error of measurement equipment is obtained by combining the individual error contributions:

$$\sigma_{AMS} = \sqrt{(U_{QAL1})^2 + (U_{QAL2})^2 + (U_{DAT})^2}$$

The total error has to be calculated separately for each measurement equipment. For quantities to be standardised (e.g. volume flow) the errors of standardisation have to be taken into account appropriately.

$$\sigma_{norm} = \sqrt{\left(\frac{273 + T + \Delta T}{273 + T} - 1\right)^2 * \left(\frac{p + \Delta p}{p} - 1\right)^2 * \left(\frac{100 - F + \Delta F}{100 - F} - 1\right)^2}$$

The mass flow error resulting is:

$$\sigma_{M_{THG}} = \sqrt{\left(\sigma_{K_{THG}}\right)^2 + \left(\sigma_{V_{Betrieb}}\right)^2 + \left(\sigma_{norm}\right)^2}$$

7 Results

7.1 Starting position based on the suitability test

The suitability test of emission measurement equipment has been carried out for many years for the classic pollutants CO, NO_x, SO_2 and others, or for reference components such as O_2. Measurement systems for waste gas volume flows are also tested in accordance with the suitability test guideline. This standard was drawn up for the testing of atmospheric measurement systems and has to be applied for this application. Measurement systems for highly compressed gases have so far not been considered in connection with emissions monitoring. As a consequence, there are no measurement systems for waste gases in the high pressure range which have been tested for suitability. However, measurement systems for the recording of gaseous fuel volumes, in particular with regard to natural gas supplies, are widely available. For these, calibration regulations apply for trading.

The following table shows the results of the latest measurement systems for waste gas volume flows which have been tested for suitability:

Table 5: Total uncertainty in accordance with QAL1 of measurement equipment tested for suitability and specified by the German Environment Ministry (BMU)

Manufacturer		Dr. Födisch	pvt technology	Fluid components	Codel International	Sick
Type		FMD 09	RG 20	MT91	V-CEM5100	Flowsick100
Measurement method		Differential pressure	Differential pressure	Convection	IR cross correlation	Ultrasound
Measurement range from	m/s	2	2	0	0	0
Measurement range to	m/s	30	25	25	50	20
Linearity	m/s	-0.196	-0.254	-0.318	0.115	0.280
Zero drift	m/s	0.000	-0.063	-0.034	0.089	-0.160
Span drift	m/s	0.173	-0.173	-0.069	-0.199	-0.160
Temperature 2)	m/s	0.058	0.300	0.000	0.306	0.020
Mains voltage	m/s	0.059	0.038	0.001	0.240	-0.060
Sample gas pressure	m/s	n.r.	n.r.	0.086	n.r.	k.A.
Standard deviation, repeat determination1)	m/s	0.127	0.240	0.082	0.507	0.400
Reference material	m/s	k.A.	0.202	0.202	0.404	k.A.
Standard uncertainty	m/s	0.30	0.54	0.40	0.80	0.54
Expanded uncertainty	m/s	0.59	1.05	0.79	1.56	1.06
Relative expanded uncertainty	% MBE	2.0	4.2	3.2	3.1	5.3
Max. value measured	m/s	26.80	16.60	19.70	18.30	14.90
relative expanded uncertainty extrapolated 120%	%	1.8	5.3	3.3	7.1	5.9

1) The larger value is used: Repeatability at span or standard deviation from repeat determination

2) The temperature dependence was tested in the range of 5 – 40 °C which is intended for indoors installations.

n.r.: not relevant; k.A.: not specified

Based on the information provided, all measurement systems listed meet the requirements of EN 15267-3. The results of volume flow measurement systems tested for suitability and listed in the table are not complete. The values from the suitability test reports in our hands were entered. Older versions of the equipment in particular, which have been tested in accordance with the standards predating EN 15267-3, are not listed.

Information on the uncertainties of the reference material is not available in all cases.

In the suitability test reports, the absolute error was applied to the measurement range stated as relative extended uncertainty of the measurement method. As the specifications of EN 16911-2 had not been available for these tests, the extended uncertainty has been related to 120 % of the maximum value measured during comparative tests in the last line of the table. The maximum uncertainty of 2 % required by EN 16911-2 is achieved only in one case. However, an error of the reference material has not been taken into account in this case.

All measurands and measurement uncertainties of the measurement systems tested for suitability relate to operating conditions at atmospheric conditions. In addition to the self-contained report of TÜV NEL at elevated gas pressures, this analysis provides a comparison of measurement results and methods.

The TÜV NEL results are related as far as possible to the standards which have to be applied for the quality-assured evaluation of emissions measurements. It may be that existing standards cannot be applied in full as measurement issues specific to the high-pressure range have to be taken into account.

7.2 Assessment of the TÜV NEL tests

Two ultrasonic meters (manufacturers GE and Sick) and one Coriolis mass flow meter (manufacturer Rheonik) were available for the TÜV NEL tests. An orifice plate which was first calibrated with water to determine the discharge coefficient was used for comparative measurements. The meters were installed in series in a test loop to allow simultaneous measurements. Pressure and temperature were also measured continuously. The gas composition, in particular the CO_2 content of the gas stream, was produced by mixing.

The meters used had not been tested for suitability. According to the manufacturers, they are suitable for process gas measurements for the in-line installation via flange connections into the gas duct.

The emphasis of the tests was on carrying out comparative measurements. The possible operating conditions in CCS gas were to be simulated in particular. Therefore, the CO_2 concentration was varied from 80 % vol. to almost 100 % vol. The tests were also carried out at various pressures from 12 bar to 20 bar. Although this does not correspond to the pressures to be expected for CCS gas, it gives an indication of the meter behaviour at high pressures. A separate measurement series was planned for the high-pressure range; however, it was not possible to carry this out as stated above.

It was not the objective of TÜV NEL to systematically determine the error contributions as for a suitability test, but to carry out a test operation of selected measurement methods and to compare them with a reference method. The individual error contributions from known suitability tests can be regarded as valid for an estimate of random errors due to equipment fluctuations.

7.2.1 QAL1 error contributions

The error contributions are estimated from the results of recent suitability tests of volume flow meters. In the following discussion, the ultrasonic method is quoted for the derivation of errors as this was tested by TÜV NEL.

Even though the same measurement methods are used for the high-pressure range, different meter types are used due to the duct dimensions and pressure setup so that the test results are applicable to high-pressure systems only to a limited extent.

An assessment of individual errors in accordance with QAL1 is not carried out here.

7.2.2 QAL2 error contributions

The systematic error contributions, determined by comparative measurements in accordance with QAL2, also contain additional uncertainty contributions from the installation position, the plant-specific waste gas composition and the operating conditions of the plant. The statistical procedure of EN 14181 and 16911-2 can be applied to the TÜV NEL tests with the previously calibrated orifice plate measurement being regarded as reference measurement.

Calibration is preceded by a functional test which also includes a linearity check. It was deduced from the TÜV NEL results that the Coriolis meter did not work linearly in the range examined. The deviations were above the deviation of residuals of 5 % to be met in accordance with EN 14181. As the meter was used in an unsuitable measurement range and it was also not possible to exclude an incorrect setting, the results of the measurements do not provide information on the suitability of this measurement method.

The results from the comparative measurements for CO_2 at 100 % vol. were assessed in accordance with EN 14181 and EN 16911-2. As the assessment has to be carried out using the unit of the measurement method, the reference mass flows were converted into a flow velocity with the unit m/s using the density and the duct cross-section. The pulse rate in pulses/s was used as the output signal of the meters.

The statistical evaluation with all parameters is provided on the following pages and the linear regressions are plotted. All individual evaluations meet the comparatively strict uncertainty requirements of EN 16911-2 with a deviation of 2 % max. For the comparative measurements with the Sick ultrasonic meter, the second value in the local density column of Table 7 of the TÜV SÜD NEL report attached as appendix has been replaced by the average of the previous and following value due to obvious implausibility.

Figure 11: GE ultrasonic meter – comparative measurements at 20 bar

Calibration function calculation and variability check					
Meter				**Sick 20 bar**	
Parameter measured				Volume flow	
Reference measurement method				ISO 5167	
Nominal K-factor				4500	pulse/m³
Output signal		0	to	1	*1000 pulses/s
ELV substitute value	**120% of maximum value**			**9.135**	**m/s**
related to waste gas conditions					
Selection of calculation method:					
Smallest standardised SRM value	$y_{s,min}$			0.887	m/s
Largest standardised SRM value	$y_{s,max}$			7.613	m/s
Difference	$(y_{s,max} - y_{s,min})$			6.726	m/s
15 % of daily limit value				1.370	m/s
Calculation method:	**Calculation as per general method**				
Parameters of calibration function:		Y = a + b X			
Intercept	**a** =			-0.001	m/s
Gradient	**b** =			**7.094**	m/s/1000 P/s
Valid calibration range:		**0**	**to**	**9.135**	**m/s**
The calibration function is valid for a range up to 20% above the maximum value ŷ.					
Variability check:					
Variability (standard deviation)	s_D		=	**0.0013**	**m/s**
- substitute limit as per 16911-2:				9.135	m/s
- required AMS quality				20	%
- as standard deviation σ_0 = P E / 1.96				0.093	m/s
- k_v for N =	12			0.987	
	$\sigma_0\ k_v$		=	**0.092**	**m/s**
$s_D \leq \sigma_0\ k_v$	→ **Variability check passed**				

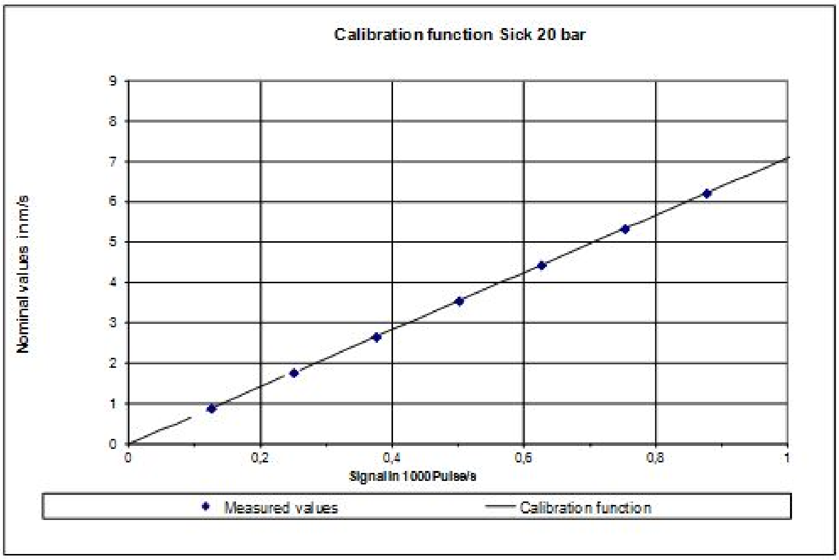


Figure 12: GE ultrasonic meter – comparative measurements at 15 bar

Calibration function calculation and variability check					
Meter				**GE 15 bar**	
Parameter measured				Volume flow	
Reference measurement method				ISO 5167	
Nominal K-factor				3600	pulse/m³
Output signal		0	to	1 *1000	pulses/s
ELV substitute value	**120% of maximum value**			**8.616**	**m/s**
related to waste gas conditions					
Selection of calculation method:					
Smallest standardised SRM value	$y_{s,min}$			0.891	m/s
Largest standardised SRM value	$y_{s,max}$			7.190	m/s
Difference	$(y_{s,max} - y_{s,min})$			6.299	m/s
15 % of daily limit value				1.294	m/s
Calculation method:	**Calculation as per general method**				
Parameters of calibration function:		**Y = a + b X**			
Intercept	a =			**-0.023**	m/s
Gradient	b =			**8.921**	m/s/1000 P/s
Valid calibration range:		**0**	**to**	**8.616**	**m/s**
The calibration function is valid for a range up to 20% above the maximum value ŷ.					
Variability check:					
Variability (standard deviation)	s_D		=	**0.0122**	**m/s**
- substitute limit as per 16911-2:				8.616	m/s
- required AMS quality				2.0	%
- as standard deviation σ_0 = P E / 1.96				0.088	m/s
- k_v for N = 12				0.987	
	σ_0 k_v		=	**0.087**	**m/s**
$s_D \leq \sigma_0 k_v$	→ **Variability check passed**				

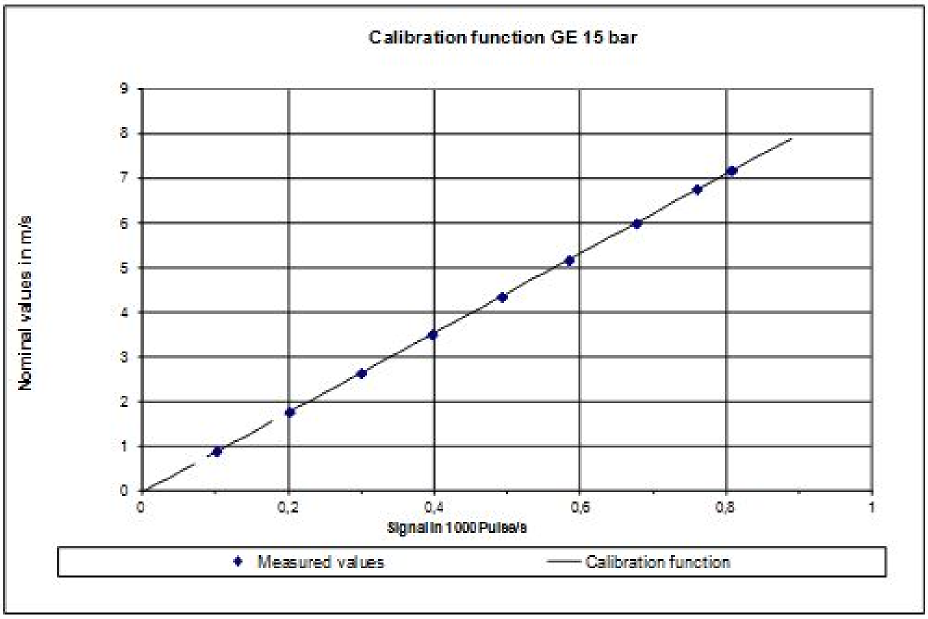


Figure 13: GE ultrasonic meter – comparative measurements at 12 bar

Calibration function calculation and variability check

Meter				**GE 12 bar**	
Parameter measured				Volume flow	
Reference measurement method				ISO 5167	
Nominal K-factor				3600	pulse/m³
Output signal		0	to	1	*1000 pulses/s
ELV substitute value	**120% of maximum value**			**8.660**	**m/s**
related to waste gas conditions					
Selection of calculation method:					
Smallest standardised SRM value	$y_{s,min}$			0.888	m/s
Largest standardised SRM value	$y_{s,max}$			7.231	m/s
Difference	$(y_{s,max} - y_{s,min})$			6.342	m/s
15 % of daily limit value				1.301	m/s
Calculation method:	**Calculation as per general method**				
Parameters of calibration function:		Y = a + b X			
Intercept	a =			-0.023	m/s
Gradient	b =			8.921	m/s/1000 P/s
Valid calibration range:		**0**	**to**	**8.660**	**m/s**

The calibration function is valid for a range up to 20% above the maximum value ŷ.

Variability check:				
Variability (standard deviation)	s_D	=	**0.0141**	**m/s**
- substitute limit as per 16911-2:			8.660	m/s
- required AMS quality			2.0	%
- as standard deviation $\sigma_0 = P E / 1.96$			0.088	m/s
- k_v for N = 12			0.966	
	$\sigma_0 k_v$	=	**0.086**	**m/s**

$s_D \leq \sigma_0 k_v$ → **Variability check passed**

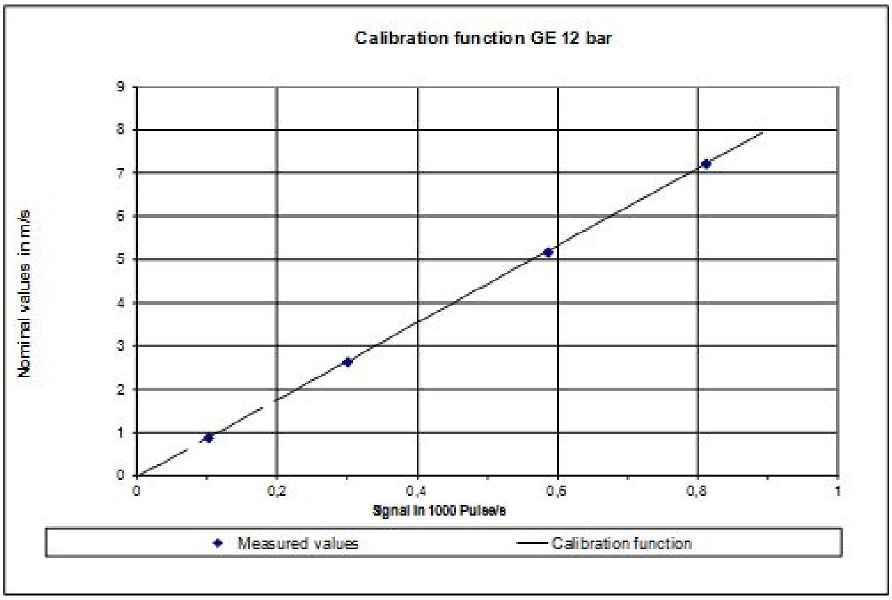


Figure 14: Sick ultrasonic meter – comparative measurements at 20 bar

Calibration function calculation and variability check

Meter				**Sick 20 bar**	
Parameter measured				Volume flow	
Reference measurement method				ISO 5167	
Nominal K-factor				4500	pulse/m³
Output signal		0	to	1	*1000 pulses/s
ELV substitute value	**120% of maximum value**			**9.135**	**m/s**
related to waste gas conditions					
Selection of calculation method:					
Smallest standardised SRM value	$y_{s,min}$			0.887	m/s
Largest standardised SRM value	$y_{s,max}$			7.613	m/s
Difference	$(y_{s,max} - y_{s,min})$			6.726	m/s
15 % of daily limit value				1.370	m/s
Calculation method:	**Calculation as per general method**				
Parameters of calibration function:		Y = a + b X			
Intercept	a =			-0.001	m/s
Gradient	b =			7.094	m/s/1000 P/s
Valid calibration range:		0	to	**9.135**	**m/s**
The calibration function is valid for a range up to 20% above the maximum value ŷ.					
Variability check:					
Variability (standard deviation)	s_D		=	**0.0013**	**m/s**
- substitute limit as per 16911-2:				9.135	m/s
- required AMS quality				2.0	%
- as standard deviation σ_0 = P E / 1.96				0.093	m/s
- k_v for N = 12				0.987	
	$\sigma_0\ k_v$		=	**0.092**	**m/s**
$s_D \leq \sigma_0\ k_v$	→ Variability check passed				

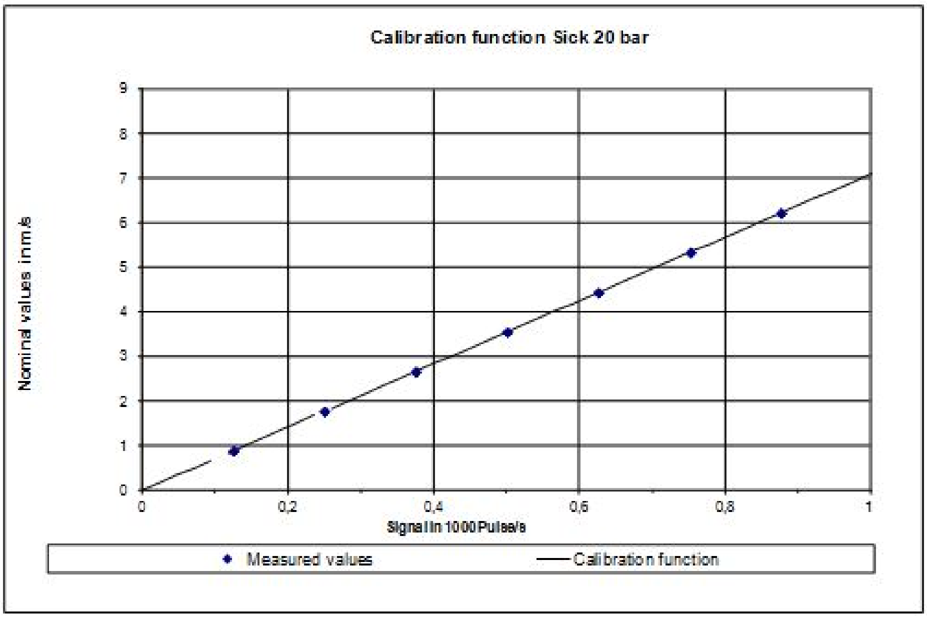


Figure 15: Sick ultrasonic meter – comparative measurements at 15 bar

Calibration function calculation and variability check					
Meter				**Sick 15 bar**	
Parameter measured				Volume flow	
Reference measurement method				ISO 5167	
Nominal K-factor				4500	pulse/m³
Output signal		0	to	1	*1000 pulses/s
ELV substitute value	**120% of maximum value**			**9.121**	**m/s**
related to waste gas conditions					
Selection of calculation method:					
Smallest standardised SRM value	$y_{s,min}$			0.891	m/s
Largest standardised SRM value	$y_{s,max}$			7.602	m/s
Difference	$(y_{s,max} - y_{s,min})$			6.711	m/s
15 % of daily limit value				1.368	m/s
Calculation method:	**Calculation as per general method**				
Parameters of calibration function:		$Y = a + b X$			
Intercept	**a** =			**-0.003**	m/s
Gradient	**b** =			**7.095**	m/s/1000 P/s
Valid calibration range:		**0**	**to**	**9.121**	**m/s**
The calibration function is valid for a range up to 20% above the maximum value $\hat{y}$.					
Variability check:					
Variability (standard deviation)	s_D		=	**0.0015**	**m/s**
- substitute limit as per 16911-2:				9.121	m/s
- required AMS quality				2.0	%
- as standard deviation σ_0 = P E / 1.96				0.093	m/s
- k_v for N = 12				0.987	
	$\sigma_0 k_v$		=	**0.092**	**m/s**
$s_D \leq \sigma_0 k_v$	→ **Variability check passed**				

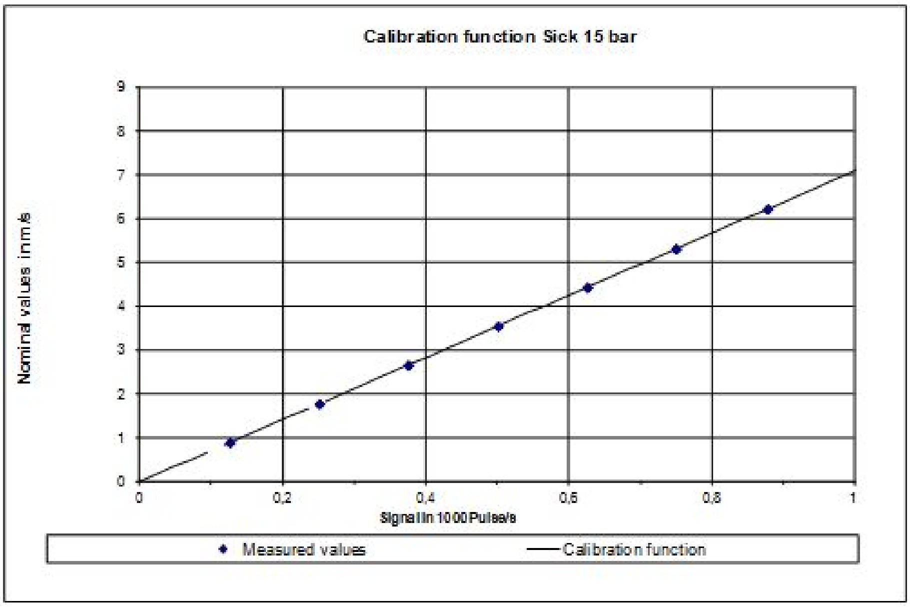
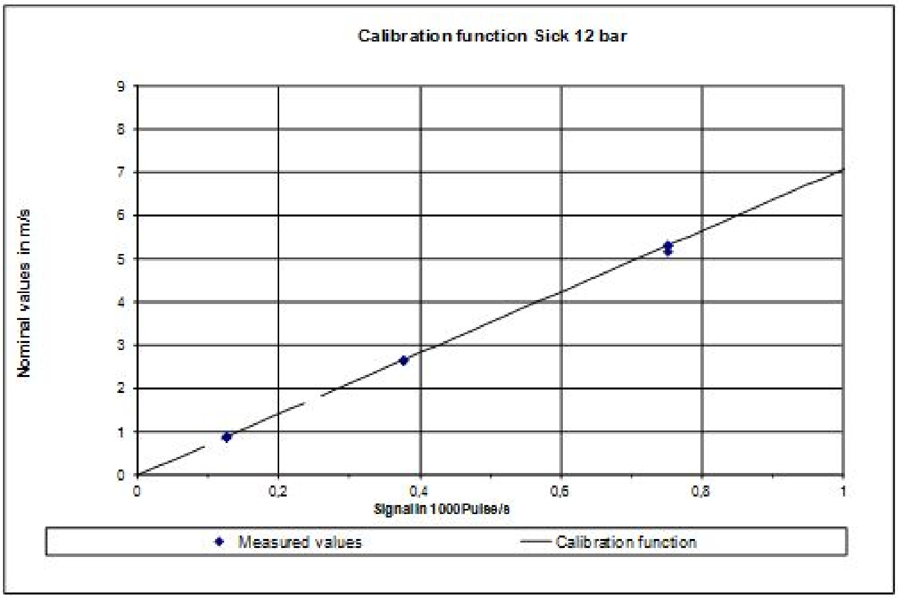


Figure 16: Sick ultrasonic meter – comparative measurements at 12 bar

Calibration function calculation and variability check

Meter				**Sick 12 bar**	
Parameter measured				Volume flow	
Reference measurement method				ISO 5167	
Nominal K-factor				4500	pulse/m³
Output signal		0	to	1	*1000 pulses/s
ELV substitute value	**120% of maximum value**			**9.142**	**m/s**
related to waste gas conditions					
Selection of calculation method:					
Smallest standardised SRM value	$y_{s,min}$			0.887	m/s
Largest standardised SRM value	$y_{s,max}$			7.639	m/s
Difference	$(y_{s,max} - y_{s,min})$			6.752	m/s
15 % of daily limit value				1.375	m/s
Calculation method:	**Calculation as per general method**				
Parameters of calibration function:			Y = a + b X		
Intercept	a =			-0.007	m/s
Gradient	b =			7.082	m/s/1000 P/s
Valid calibration range:		0	to	**9.142**	**m/s**
The calibration function is valid for a range up to 20% above the maximum value ŷ.					
Variability check:					
Variability (standard deviation)	s_D		=	**0.0407**	**m/s**
- substitute limit as per 16911-2:				9.142	m/s
- required AMS quality				2.0	%
- as standard deviation σ_0 = P E / 1.96				0.093	m/s
- k_v for N =	12			0.966	
	$\sigma_0\ k_v$		=	**0.090**	**m/s**
$s_D \leq \sigma_0\ k_v$	→ **Variability check passed**				



It was not possible to carry out the evaluation of the variability test with the results of the mixed gas tests at 80 % vol. and 90 % vol. CO_2 as the base data required were not provided in detail. However, when considering the deviations quoted by TÜV NEL for the individual measurements it is to be expected that the variability required can be met statistically for a sufficient number of comparative values. The confidence interval, quoted as standard deviation, gave a maximum value of 0.04 m/s.

7.3 Assessment of the Possible Uncertainty

The error component resulting from the systematic deviations of the measurement system as generally determined by QAL2 can be derived from the above tests.

The uncertainty contributions from the suitability test are listed in the following table. They are listed in the other columns in accordance with random and systematic error contributions. The random errors of QAL1 are used as inputs for the drift check in accordance with QAL3. The other error contributions are determined specifically for the relevant location by the QAL2 calibration.

Table 6: Combined uncertainty contributions from suitability test and calibration

Manufacturer		QAL1	QAL2	Flow
Type		Flowsick100	Flowsick100	
Measurement method		Ultrasound	Ultrasound	
Measurement range from	m/s	0	0	
Measurement range to	m/s	20	20	
Linearity	m/s		0,040	
Zero drift	m/s			
Span drift	m/s	-0.160		
Temperature	m/s	0.020		
Mains voltage	m/s	-0.060		
Sample gas pressure	m/s	k.A.		
Standard deviation, repeat determination	m/s	0.400		
Reference material	m/s			
Standard uncertainty	m/s	0.44	0.04	0.44
Expanded uncertainty	m/s	0.85	0.08	0.86
Relative expanded uncertainty	% MBE	4.3	0.4	-
Max. value measured	m/s	14.90	9.00	14.90
Relative expanded uncertainty Extrapolated 120 %	% MBE	4.8	0.7	4.8

For systematic error contributions it has to be taken into account that these include additional uncertainty contributions from the place of installation, plant-specific gas composition and operating conditions of the plant. The systematic error contributions which are specific to the plant must be determined with a calibration by an accredited measurement institute, for the first time after commissioning and then every three years. If the maximum uncertainties required are not achieved, it is possible to minimise the statistical error by optimising the measurement location and the measurement equipment or by optimising the calibration method by optimum application of reference methods and number of comparative measurements.

The random error contributions are fluctuations due to environmental effects which cannot be avoided by the measurement system and are stated as the QAL1 standard deviation. If the operator duties in accordance with QAL3 of EN 14181 are met, observance of the standard deviation is guaranteed. The standard deviation derived from the suitability test is used as the starting value for the intervention limit for readjustment of the measurement equipment. The standard deviation and thus the intervention limit may, however, be over- or underestimated and can be determined afterwards individually based on the real operational fluctuations.

The QAL3 records of the ongoing operation are then used as proof for this uncertainty contribution to the total uncertainty of the measurement equipment. The total uncertainty of the measurement equipment for concentration and the combination with the measurement of the waste gas volume (gas velocity and duct cross-section) are calculated in accordance with the equations listed in section 6.9.

However, it is not yet possible to give a reliable estimate of the total error, as there are no results on the QAL1 component of the meter types used.

7.4 Concentration Measurement by Speed of Sound

This part of the tests in the TÜV NEL report illuminates a possibility, to which so far little attention has been paid, of determining the concentration of CO_2 from the dependence of the speed of sound on the density of the medium. As CO_2 has a high density compared to the other waste gas components this in turn is an indicator for the CO_2 concentration. It was not possible to provide a direct comparison with a concentration measurement, but it can be assumed from the comparative assessments of the density differences from the speed of sound that a reliable CO_2 determination is possible. Even if the measurement uncertainty required should not be achieved, the assessment of the speed of sound can provide an indication of changes in concentration and be used for the plausibility check of other parameters measured.

7.5 Conclusions and Recommendations

7.5.1 Gas volume flow

The results of the comparative measurements can meet the variability requirements of the standard for the calibration of volumetric flow meters. The investigations confirmed this for the ultrasonic meters of various manufacturers. When the optimised conditions are maintained, as is the case in test operations, systematic deviations are likely to be of minor importance in the assessment of the overall error.

No examination of the suitability test criteria are available. It is expected that at least the experimental values from suitability tests will be achieved by meters for industrial installations. As the applicable standard, currently of 2013, makes similarly high requirements on gas volume, it is now up to the manufacturers to further optimise their devices. This will lead to further reductions of systematic and random deviations.

The tests described here were carried out up to 20 bar. It was not possible to carry out the planned further tests due to technical difficulties with the test facility and the prioritised completion of the project by the Client. Among other things, operation in the high pressure range up to 150 bar was planned, as is planned for real CCS operation.

In addition, operating with targeted contaminants was planned for the second part of the tests. The behaviour, in particular, of various trace components in the transition area of phase boundaries which are clearly different from the phase transitions of CO_2 would have been of great interest. The boundaries in the CO_2 phase diagram can be shifted significantly by contaminants which would increase the likelihood of a two-phase stream.

Entrained water vapour in particular can form carbonic acid with the CO_2 and thus promote corrosion. The contamination should be kept as low as possible when CO_2 is separated.

CCS gas must be highly compressed for transport. For this, the gas must first be dehumidified to a minimal residual concentration of water vapour as the water vapour would freeze out and cause a blockage of pipe fittings. The use of gas coolers to condition the waste gas is recommended even for dry gas.

The Coriolis meter intended for testing could not deliver any results. The meter had an unsuitable measurement range. In principle, Coriolis meters have the advantage that they output mass flow direct as measurand. Thus additional uncertainties from the determination of temperature and density are removed.

The reference method for the calibration of gas volume meters in the waste gas of industrial plant is the measurement using the differential pressure method or using vane anemometers in accordance with EN 16911-1 [10].The probe is introduced into the gas duct through several sampling ports for the purpose of network measurements. These methods in the application described are not suitable for high-pressure ducts. There is a requirement for the standardisation of suitable reference measurement methods for the QAL2 calibration.

7.5.2 Concentration measurement in waste gas

There is no practical experience with real compressed gas with enriched CO_2 contents. The test with gas sampling using compressed gas was planned for the second test part. Separation effects of the gas have to be expected. It can be assumed that as fast a relaxation to atmospheric conditions as possible can largely prevent this.

There is no measurement equipment tested for suitability with a measurement range above 25 % vol. CO_2. As suitability tests entail high costs for the manufacturers of measurement equipment they will become active only once a market arises for this application.

The assessment of the speed of sound for the determination of the CO_2 concentrations is an interesting option which should be examined in more detail.

There is no reference method for the calibration of CO_2 measurement equipment specified in a standard. Analogous to CO measurement, which is comparable with regard to the measurement method, NDIR measurement systems could be used for this, too.

A high uncertainty contribution is provided by the test gas used as reference material. Lower uncertainties certified by the manufacturers would be of great importance to minimise the uncertainty contribution.

An inversion of the measurement range for highly concentrated concentrations improved the measurement sensitivity. Pure CO_2 is used in the cell as reference gas which corresponds to physical zero. A measurement signal occurs for an appropriately reduced CO_2 content. The measurement range in this case goes from 100 % vol. to, ideally, 80 % vol. This increased the measurement sensitivity compared to the equipment tested five times. Some manufacturers offer this measurement range for special applications. No equipment was available for this test.

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