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## Monitoring real time, in-line variations of noble gas concentrations during CO<sub>2</sub> capture operations by means of a portable mass spectrometer

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### Abstract

In the ICO<sub>2</sub>P-project the overall aim is to develop an innovative and cost-effective monitoring scheme for CO<sub>2</sub> capture and storage operations, implementing new methods for in situ noble gas measurements. The first step is to establish a basis for fluid source identification by recording temporal variance of noble gas composition in CO<sub>2</sub> product. Studies of noble gases related to CCS typically include few, single point samples. In ICO<sub>2</sub>P, a portable mass spectrometer (i.e. miniRUEDI) is utilized to directly measure real time variability of the noble gas content in CO<sub>2</sub> gas streams at operating CCS facilities. The first study was performed at the Technology Centre Mongstad (TCM) in Norway, a large-scale test facility for post-combustion CO<sub>2</sub> capture operations. During an open scientific test campaign for amine-based capture (TSA-MEA), noble gases (He, Ar, Kr) as well as CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> concentrations in the CO<sub>2</sub> product stream were recorded every 10 to 15 minutes during a 5-day period. He concentrations (<0.001ppm) were depleted post-capture and too low for temporal variation measurements in the CO<sub>2</sub> product line. Ar concentrations (0.15 – 0.65 ppm) were significantly higher and temporal variation was successfully recorded in the CO<sub>2</sub> product line. Ar was found to be sensitive to capture operations, e.g. CO<sub>2</sub> recycling ratio. This new approach will provide knowledge of the uniqueness and variability of inherent noble gas fingerprints and depletion/absorption during CCS operations and provide grounds for comparison between fluid origins needed in leakage detection schemes at CO<sub>2</sub> storage sites.

*Keywords:* CO<sub>2</sub> storage; CO<sub>2</sub> capture; CCS; noble gases; monitoring;

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## 1. Introduction

During a recent feasibility study [1], to assess the potential for real-time, semi-continuous noble gas monitoring, data were collected from CO<sub>2</sub> capture operations at the Technology Centre Mongstad (TCM) in Norway (Fig. 1), using a novel method for quantitative gas composition measurement. The overall aim has been to contribute towards developing innovative and cost-effective monitoring schemes for CO<sub>2</sub> capture and storage operations, work that is now part of an ongoing research project - the ICO<sub>2</sub>P-2 project [1] during 2018-2021.

By recording temporal variance of noble gas composition in CO<sub>2</sub> capture products, the inherent geochemical fingerprint can be evaluated with respect to the potential for source identification at prospective storage sites (i.e. differentiation of sources at CO<sub>2</sub> seepage sites or natural variations in marine and terrestrial environments). Studies so far typically include only a few, single point samples, and there is a clear need for more background data on gas compositions and better sampling strategies to ensure safe storage and reliable leakage detection. The miniRuedi [2] portable mass spectrometer has the capacity to measure low concentrations (i.e. partial pressures) of He, Ar and Kr, as well as CO<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub> and other relevant chemical substances with high accuracy at sample intervals of < 15 minutes. This technology proved suitable for monitoring fluctuations in some components of the CO<sub>2</sub>-product composition, as tested during an open scientific test campaign for post-combustion capture processes; amine-based temperature swing absorption (TSA), at TCM in summer 2017.

This data set, and further work, will provide important knowledge on absolute variability in CO<sub>2</sub> product from complex and mixed sources. During capture operations and before storage of CO<sub>2</sub> can commence, there is a need to document variability, and to evaluate the inherent compositional signature (and the potential need for adding tracers). This approach will allow for source-specific identification of fluids; differentiating injected (anthropogenic) CO<sub>2</sub> from natural (methanogenic / biogenic) CO<sub>2</sub> rich gases at potential leakage points.



Fig. 1. Technology Centre Mongstad (TCM), Norway [Photo © Equinor] DA amine plant with CHP flue gas inlet from the front, and the high absorber tower in the middle. “Captured” CO<sub>2</sub> product outlet and sample point towards the right.

## 2. Noble gases as tracers in CCS (and EOR)

Reliable monitoring is a prerequisite for safe, long-term storage and public acceptance of CCS. Terrestrial noble gases (i.e. He, Ne, Ar, Kr, Xe) appear to be suitable natural tracers for monitoring and understanding CO<sub>2</sub>-rich gas systems [3]. They are chemically inert and non-degradable. And in contrast to several commonly applied chemical tracers (e.g. PerFluoroCarbons), inherent noble gases are not harmful to the environment and bring no additional cost. The concept of using noble gases for monitoring CO<sub>2</sub> projects has been demonstrated at small-scale onshore facilities, and noble gas data proved to be crucial evidence to rule out an alleged leakage incident at the Weyburn project [4].

However, there are still knowledge gaps: studies so far typically include only a few, single-point samples, and there is a clear need for better data on gas compositions and variability.

To understand large-scale reservoir dynamics and fluid mixing at CO<sub>2</sub> injection sites and along possible leakage paths, experience from research related to multi-phase hydrocarbon systems have to be used and adapted to the scientific case of CCS. Formation water in deep, saline aquifers will have a unique noble gas signature based on a blend of an atmospheric component (stable contents of <sup>20</sup>Ne, <sup>36</sup>Ar, <sup>84</sup>Kr), a deep mantle component (mostly supplying <sup>3</sup>He) and a crustal radiogenic component (production of <sup>4</sup>He, <sup>21</sup>Ne, <sup>40</sup>Ar). The signature is a function of time and dependent on the in-situ lithology [5]. Crustal <sup>4</sup>He is supplied from radiogenic decay of U and Th in minerals, and <sup>40</sup>Ar is produced by radioactive decay of <sup>40</sup>K. The mixing ratios of meteoric, mantle and crustal components may yield information about residence times and fluid mixing. E.g., it was found that seepage of methane causes depletion of <sup>20</sup>Ne and <sup>36</sup>Ar relative to <sup>4</sup>He by partitioning, as the heavier noble gas species are more soluble in methane than in water [5]. Exchange between groundwater and oil phase may also be detected as increased <sup>20</sup>Ne and <sup>36</sup>Ar abundance in oil, as described for the Magnus Field in the British North Sea [6]. Injected CO<sub>2</sub>-rich fluid will also interact with formation water and/or hydrocarbon phases present in a storage reservoir. A recent tracer test at the Cranfield enhanced oil recovery (EOR) field in the US, adding Kr and Xe, showed noble gases to be stripped from formation water and into the CO<sub>2</sub> phase [7]. Mapping of the background noble gas abundance before injection is of utmost importance to characterize the natural gas composition and spatial distributions prior to CO<sub>2</sub> injection. This will improve the understanding of CO<sub>2</sub> trapping mechanisms and oil/water/gas partitioning in reservoirs, and form the grounds for comparison needed in leakage detection schemes.

### 2.1. Compositional variability in captured CO<sub>2</sub>

Norway is currently at the forefront in developing CCS, along with Canada, Australia, USA and China. With two active storage sites and a national plan to establish another, larger-scale offshore storage site at Smeaheia, there is an imminent need to prepare reliable, cost-effective and long-term monitoring programs. Noble gas finger-printing can provide an applicable solution, but there is a significant knowledge gap concerning the inherent signature of CO<sub>2</sub> from various capture processes.

At the operative Sleipner and Snøhvit sites, inherent CO<sub>2</sub> from fossil sources (natural gas reservoirs) is captured (as part of the gas processing) and re-injected into a storage formation (saline aquifer). Such single-source storage schemes are expected to display the least degree of temporal variation in the noble gas compositions of injected gas. The noble gas signature of a given natural gas accumulation is related to long-term, slow accumulation rates of e.g. <sup>3</sup>He, <sup>4</sup>He, <sup>21</sup>Ne, <sup>40</sup>Ar in a given geological setting. Lateral or vertical compositional gradients in reservoirs related to the lithology and contact time with fluids in traps and along migration paths, may be documented as compositional changes during production. However, these changes are expectedly subtle, compared to complex mixed-source and post-combustion schemes. At the Technology Centre Mongstad (TCM) the source is mixed, and natural gas from several reservoirs are combusted before CO<sub>2</sub>-rich flue-gas enters the capture facility. CO<sub>2</sub> is captured from a combination of flue gases; (1) from a combined cycle gas turbine (CCGT) based heat and power plant (CHP) or (2) the residual fluid catalytic cracker (RFCC) at the Equinor refinery at Mongstad. At the CHP plant large quantities of gases from different fossil sources are combined, but after initial mixing and combustion, the signature of the flue gases are expected to become relatively homogenous within a few days. Then, with addition of residual refinery gas, the compositional variability is expected to increase. Further, the combustion process will add an atmospheric component.

Depletion of the radiogenic/nucleogenic components of reservoir derived noble gases occurs during combustion and capture [8]. In the product line recirculation rates, addition of different solutes with given solubilities for the gases and their isotopes under varying pressure and temperature conditions will affect noble gas contents. In this study, we attempt to document temporal changes, and the next step is to interpret and decipher the relative effects of capture processes on noble gas fingerprinting. Additionally, documenting variation in the fossil gas feed is highly relevant in evaluating the traceability of mixed-source gas in future storage schemes, involving captured CO<sub>2</sub> also from other industries (e.g. cement, ammonia, waste incineration, biogas). E.g. the presented storage scheme for Smeaheia involves storage of CO<sub>2</sub> from mixed sources, after post-combustion capture.

### 3. Methodology

#### 3.1. Capture processes at TCM

The Technology Centre Mongstad (TCM) is a large-scale test facility for CO<sub>2</sub> capture operations. This study was conducted in July 2017 during an open scientific test campaign for post-combustion capture processes, using amine-based temperature swing absorption (TSA) [e.g. 9, 10, 11]. Monoethanolamine (MEA) is used as solvent for CO<sub>2</sub>. The combined cycle gas turbine and power plant is run with reservoir gas from different fields in the North Sea mixed with a fraction (up to 50 %) of residual gases from the nearby refinery. Flue gas is fed into the TCM plant, cooled, run through the absorber, before CO<sub>2</sub> is stripped off by heating the solvent and vented to a safe location in a dedicated vent stack (Fig. 2). During the test period, the capture plant was run with flue gas from the CHP plant, with a CO<sub>2</sub> concentration of approximately 4 vol%. In addition, recycling (i.e. return of CO<sub>2</sub> product back to feed gas upstream absorber) was performed, increasing the CO<sub>2</sub> content to mimic concentrations similar to coal combustion capture (Fig. 2).

#### 3.2. Portable mass spectrometer

The adapted mass spectrometric technology for analyzing extremely low concentrations and the isotopic fractionations of He, Ne, Kr, Xe, Ar in water and gas is available only in few laboratories worldwide, with the research laboratory at Eawag/ETH (Zürich) being one of the pioneers in this field.

The miniRuedi (Fig. 3) allows for semi-continuous gas analysis (i.e. partial pressures), and may be used to measure noble gas concentrations. It consists mainly of two vacuum pumps (DP, TP) and a quadrupole mass spectrometer (QMS) with two detectors (Faraday and Multiplier) with different sensitivities. In contrast to fixed laboratory units, no purification by e.g. cryogenics is carried out, which reduces the detection limits, but allows for on-site measurements and smaller instrument units [2]. The instrument has several inlet ports such that a standard gas for calibration and multiple samples can be measured subsequently and automatically without changing the setup. The consumption rate of sample gas is negligible low compared to passing gas streams.

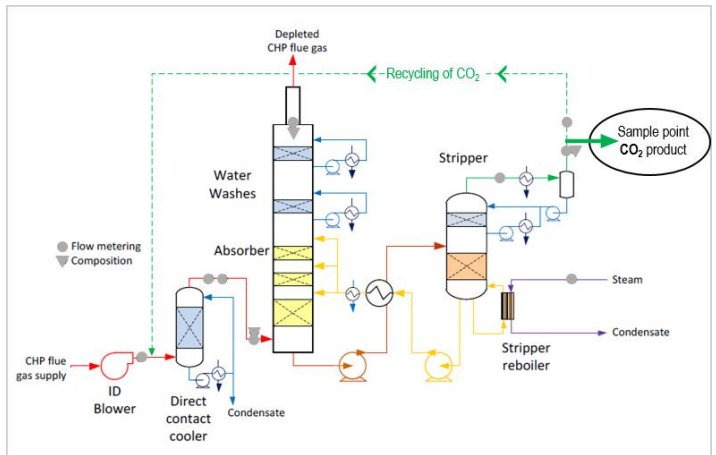


Fig. 2. Post-Combustion CO<sub>2</sub> capture at the Technology Centre Mongstad during TSA-MEA test campaigns. A mobile mass spectrometer was connected to the CO<sub>2</sub> product line. Modified from Thimsen et al. [9]

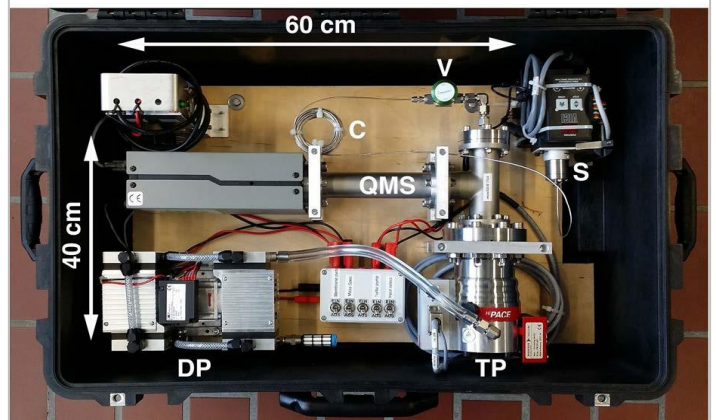
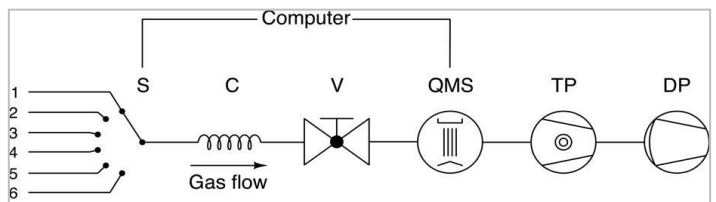


Fig. 3. The miniRuedi portable mass spectrometer (figure from Brennwald et al. [2]) set up with 6-port inlet selector valve (S), capillary (C), inlet valve (V), quadrupole mass spectrometer (QMS), turbomolecular pump (TP), and diaphragm pump (DP).

The instrument has several inlet ports such that a standard gas for calibration and multiple samples can be measured subsequently and automatically without changing the setup. The consumption rate of sample gas is negligible low compared to passing gas streams.

### 3.3. Sample set-up

A miniRuedi [2] mass spectrometer was connected to the outgoing CO<sub>2</sub> product line, downstream the overhead condenser of the CO<sub>2</sub> stripper (Fig. 2). This stream is water-saturated, and the slip-stream to the instrument was passed through a dryer to avoid the risk of condensation in the instrument. A pressure regulator was mounted between the sample point and the membrane inlet to decrease the inlet pressure to atmospheric pressure. This inlet pressures were fairly constant and recorded with a pressure sensor. The instrument was mounted in less than 1 hour, and ran continuously during a 5-day test period. The analytical sequence was set to repeating cycles of one air-standard analysis block (calibration), followed by three CO<sub>2</sub> output stream sample analysis blocks. An ambient air sample analysis block was added intermittently to remove residual CO<sub>2</sub> from the ion source. The analysis blocks lasted between 10 and 15 minutes depending on the number of components measured. During the test He, H<sub>2</sub>O, Ne, N<sub>2</sub>, O<sub>2</sub>, Ar, CO<sub>2</sub> and Kr were measured. In this way, a unique, semi-continuous data series of gas content was collected and suitable measurement routines were established. Single samples were gathered for lab analysis of noble gas isotopes.

## 4. Results

The instrument ran steadily throughout the sampling period. However, as this was a feasibility study, parameters such as air-calibration and sampling intervals as well as the selection of analyzed components were tweaked and tested underway. Absolute concentrations of CO<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub> were compared with measurements performed by TCM (in-line gas-chromatography). Low concentrations of noble gases throughout the measuring campaign confirm depletion during capture. Kr and Ne were excluded after initial sampling tests, as their partial pressures were below the detection limit. He was too low (< 0.001 ppm) throughout for proper quantification with the miniRuedi, as peak variation could not be deciphered from background. This was confirmed in new, preliminary data analysed after the GHGT poster presentation, and thus He plots are excluded from this final summary. Further studies of single samples and continuous measurement of pre-capture variation (source inlet) are ongoing.

Ar (150 – 650 ppm) contents were significantly higher compared to He, Kr, Ne, and was measured throughout the 5-day sampling period (Fig. 4). Some significant changes were observed (i.e. sudden increase/decrease). The

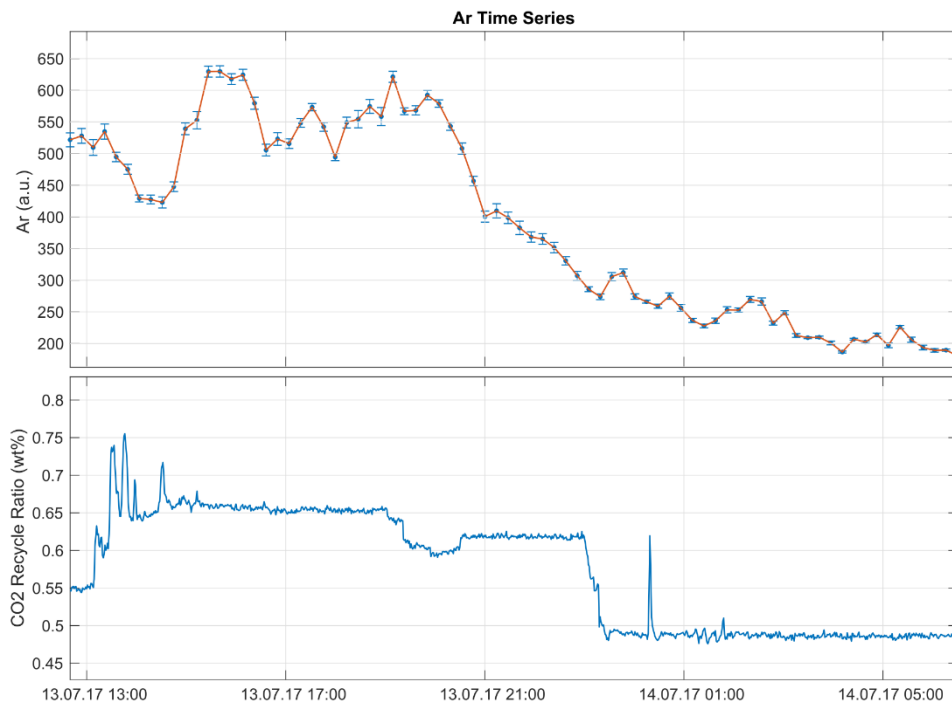


Fig. 4. Measured Ar concentrations (ppm) during the test period 10.07. – 15.07.2017 (upper) displaying co-variance with CO<sub>2</sub> recycle ratio (wt %) at the TCM plant (lower).

analytical error at sampling intervals of 10 - 15 minutes was acceptable, but the standard gas (air) used for calibration was found to be sub-optimal. Ar concentrations appear to be sensitive to changes in the recycle ratio and the capture process (Figs. 4, 5). Preliminary results from single samples confirm that He content is lower in the refinery gas compared to in the natural gas source, and concentrations are expected to vary according to relative contributions from natural gas versus refinery gas (Fig. 6). An observed decline in measured Ar concentrations coincided with reduction of CO<sub>2</sub> recycling in the line, a scheduled process change (Fig. 4).

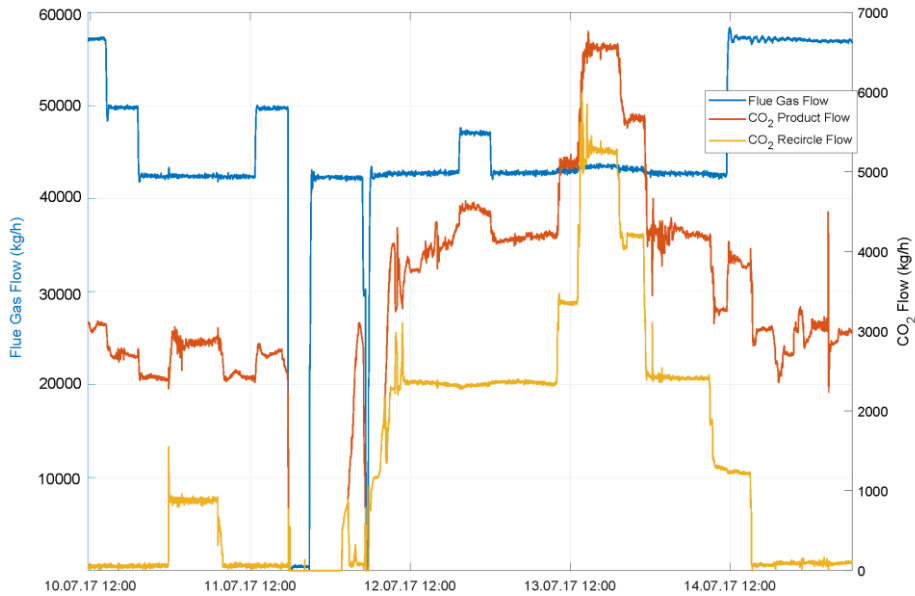


Fig. 5. Gas flows (kg/h); flue gas, CO<sub>2</sub> product and recycled CO<sub>2</sub>.

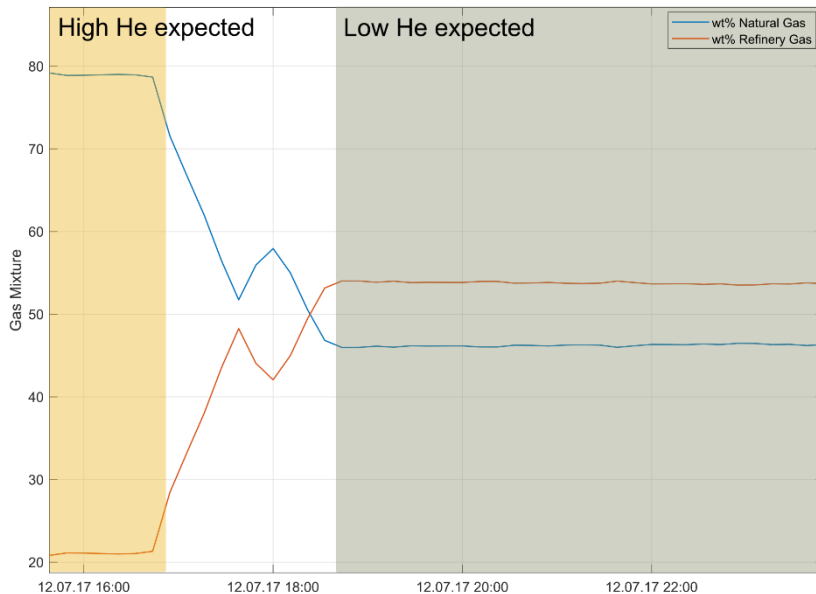


Fig. 6. Change in flue gas composition (wt % refinery gas vs. natural, detail from Fig. 5). Single samples indicate lower He concentrations in RFCC flue gas, such that concentration changes are expected for different mixing ratios.

## 5. Discussion

The test was successful in that the miniRuedi instrument ran continuously and variation in Ar concentrations were observed and documented. Up to 50 % change in relative concentrations of Ar was observed in the course of 5 days. This shows that there is noble gas variability, and that continuous monitoring is useful to ensure representative sampling in evaluation of inherent fingerprints and traceability. Preliminary single sample results show that concentrations are detectable with our technique before absorption (capture). During gas combustion and in the RFCC process, contamination with air occurs.

Assuming that tests during the capture processing (e.g. recycling) in a regularly working plant are not occurring, variations due to the capture process are expected to be minor. Thus noble gas variation related to source rather than process changes should be measured/detectable at the inlet. This is evaluated in ongoing studies.

The approach of in-line monitoring with a miniRuedi instrument is straightforward. However, optimization is necessary in order to reduce analytical uncertainty. Sample intervals of ~ 10 minutes were found suitable with respect to signal reading time and peak heights, and relative to sample resolution (gradual compositional changes). A customized calibration gas more similar to the CO<sub>2</sub>-product should be used in future tests for improved accuracy. Absolute variability in Ar concentrations was registered, and may be used to guide sampling for further chemical analysis and noble gas isotopic signature, ensuring a representative data set of single samples.

TCM is a test facility, and thus the CO<sub>2</sub> product is not stored. There are, however, plans to establish a full value CCS chain in Norway, including storage of CO<sub>2</sub> captured post-combustion [12]. Storage of CO<sub>2</sub> from multiple sources (e.g. fossil fuels, cement, waste incineration) and different capture operations are challenging. Semi-continuous noble gas analysis may allow for pre-injection gas fingerprinting. With regards to detectability at potential leakage sites and separation of different anthropogenic type sources in reservoirs, however, some additional tracer gas may have to be added. At single-source sites (e.g. Snøhvit, Utsira), inherent fingerprints may suffice for source identification. For evaluation of source variability and the effect of the capture process on noble gas signatures, both the flue gas supply (inlet) and CO<sub>2</sub> product (outlet) should be monitored simultaneously. Multiple capillary inlets to the miniRuedi instrument allows for semi-continuous monitoring of several sample points. Total variation estimates are useful to guide sampling for isotopic analysis.

Ar concentrations displayed significant variation. During the Ar decrease shown in Fig. 4 the recycling rate was adjusted. Even though this is a change that may not occur in a running large-scale capture site, the dramatic decrease emphasizes that there is a response in the noble gas assembly related to capture process changes. During the test period measurements indicate that noble gases were heavily depleted after capture. He concentrations are significantly lower than atmospheric concentrations (~ 0.00524 hPa). Alternative sampling techniques, e.g. [13], may be tested in further research for gases currently below detection limit (i.e. He, Ne, Kr). Monitoring in-line variation and correlating with isotopic fractions from previous samples will reduce the need for costly and time-consuming lab analysis.

## 6. Conclusions

The utilization of noble gases as added and/or natural tracers in the context of CO<sub>2</sub> storage monitoring is rather new. As CCS is being upscaled and put into practice, the need for combined and improved monitoring techniques is becoming evident. This feasibility study found that the miniRuedi [2] allows for frequent and accurate measurements of Ar abundance in captured CO<sub>2</sub> from a *post-combustion* like facility (TCM). Preliminary single sample analyses indicate detectability also for continuous measurements of variation in He in the flue gas supply (source) before absorption and depletion during *post-combustion* capture. At *pre-combustion* sites, however, contamination with air is expected to be significantly lower, and considering He concentrations (enriched during radiogenic production) measured in North Sea gas fields [6], monitoring temporal variations for He in the CO<sub>2</sub> product at *pre-combustion* capture sites is feasible. Documentation of variability in live gas streams and guided follow-up sampling for isotopic analysis in the lab will provide an important basis for consideration of noble gas fingerprints in monitoring schemes and leakage detection. This is a new approach that will provide knowledge of the uniqueness of noble gas fingerprints in the product stream from hydrocarbon production, CO<sub>2</sub> capture operations and in the injection line for CO<sub>2</sub> storage.

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